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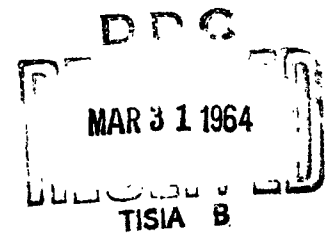
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DMIC Report 195
January 10, 1964

PROPERTIES OF COATED REFRACTORY METALS



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DMIC Report 195
January 10, 1964

PROPERTIES OF COATED REFRACTORY METALS

by

W. A. Gibeaut and E. S. Bartlett

to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio

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PROPERTIES OF COATED REFRACTORY METALS

SUMMARY

This report summarizes the information generated since the middle of 1961 on the chemical, physical, and mechanical properties of refractory metals that are coated with oxidation-resistant coatings of advanced-experimental or commercial status. It is a supplement to DMIC Report 162, "Coatings for the Protection of Refractory Metals from Oxidation", dated November 24, 1961. Recent data on specific silicide- and aluminide-type coatings for columbium, molybdenum, tantalum, and tungsten and their alloys reflect general advances in coating quality and performance, understanding of the behavior of coated systems, and more complete realization of the problems associated with the use of coated hardware.

Programs to provide comparative evaluations of coatings on columbium and molybdenum alloys have pointed up some of the relative merits and deficiencies of the various coatings. Properties that have been studied and evaluated in recent investigations have included the following:

- (1) Oxidation lives at various temperatures and pressures
- (2) Degradation in low-temperature ductility of substrates by coatings or coating processes.
- (3) Degradation of mechanical properties by oxidation exposure (thermal stability)
- (4) Effects of strain at low and high temperatures on protectiveness of coatings
- (5) Stress rupture and creep data of coated systems
- (6) Fatigue properties of coated systems
- (7) Emittance of coatings.

Although there is no "ideal" coating for a given application, the data now available may permit selection of a coating or coatings based on a balance of performance features such as those listed above. Continued detailed evaluation and general comparative programs are expected to greatly improve the ability to select a coating-substrate system best suited for given design requirements.

Generally, the areas involving coated tantalum and tungsten alloy substrates are not so well developed; there are fewer coatings available and data are more limited.

INTRODUCTION

This report presents chemical, physical, and mechanical properties of refractory metals that are coated with advanced experimental or commercial oxidation-resistant coatings, and supplements the second half of DMIC Report 162, "Coatings for Protection of Refractory Metals From Oxidation", which dealt with the characteristics of coating systems. The information presented covers the period from the middle of 1961 to date. The coatings considered are silicides, aluminides, and the liquid tin-aluminum system. Because they represent a different class of thermal protection system, thin oxide coatings and thicker metal-reinforced oxide layers are not covered. The report is divided into four sections, covering coatings for columbium, molybdenum, tantalum, tungsten, and their alloys. Coating processes are described summarily for those systems for which information is available.

The primary intention is to present performance data on coated refractory metal systems. Interpretations, summarizations, or conclusions have been added where warranted. Frequently, however, the interpretation of the data is complicated by factors such as the scatter of data in test results, the tentative nature of data obtained from progress reports, and lack of supporting information in references; in these instances evaluation of data has been left to the reader.

Strength data, such as yield, tensile, and stress-rupture strengths, of coated specimens generally are calculated using the thickness of the uncoated sheet. The actual thickness of substrate remaining after a coating is applied may be reduced by up to 1 mil per side for diffusion interaction with the coating, which is equivalent to a 5 to 20 per cent reduction in actual substrate thickness when considering sheets up to 30 mils thick. Hence, apparent strength losses of from 5 to 20 per cent (depending on sheet thickness) for coated versus uncoated thin sheet may not be significant when considering only the effect of the coating on the substrate. Unless the method of calculating strength is described it can be assumed that it is based on sheet thickness prior to coating.

COATINGS FOR COLUMBIUM AND COLUMBIUM-BASE ALLOYS

Numerous columbium-base alloys have been developed to a commercial status. Those with which coatings investigations have been concerned and for which data are described in this report include:

B66	Cb-5Mo-5V-1Zr
Cb-1Zr	Cb-1Zr
C103	Cb-10Hf-1Ti
C129	Cb-10W-10Hf
Cb752	Cb-10W-2.5Zr
D14	Cb-5Zr
D31	Cb-10Mo-10Ti
D36	Cb-10Ti-5Zr
D43 (X110)	Cb-10W-1Zr
F48	Cb-15W-5Mo-1Zr
FS82	Cb-33Ta-1Zr
FS85	Cb-27Ta-10W-1Zr

Interest is increasing in coated columbium alloys because alloys higher in strength and more fabricable than former ones are being made available. Research and development on the coating of columbium alloys now equals or exceeds that for molybdenum alloys. The competitiveness of columbium alloys for applications in the temperature range originally dominated by molybdenum alloys makes it necessary to compare the performance of coated high-strength alloys of both types.

Although much information is available concerning oxidation resistance and mechanical properties of coated columbium alloys, there is a lack of emittance data for even the better coatings.

Data for Individual Coatings

TRW Cr-Ti-Si Coating

During the past 2 years Thompson Ramo Wooldridge has endeavored to make its process for applying the Cr-Ti-Si coating more amenable to coating large pieces of hardware and to improve coating performance. They have conducted extensive evaluations of the coating on a variety of columbium alloys.^{(1)*} The conditions reported most recently for applying the coating are given below in chronological order.^(1,2)

- (1) Titanium precoat - 6 hours at 1900 F under 10^{-2} mm pressure in a titanium-sponge pack containing KF activator
- (2) Cr-Ti codeposition - 8 hours at 2300 F under 1.5 mm pressure in a 50Cr-50Ti metal pack containing KF activator
- (3) Siliconizing - 4 hours at 2000 F under 10^{-2} or 1.5 mm pressure in a silicon pack containing KF activator.

The chief attribute of the titanium precoat is that it maximizes oxidation life of the coating in the temperature range from 1200 to 1800 F. It frequently is eliminated if 25 to 100 hours' protection is all that is needed in this low-temperature range. Siliconizing can be done under 150 mm argon pressure but preliminary data indicate that the oxidation resistance of the resulting system at 1800 F is less than that achieved by siliconizing at the lower pressures.⁽³⁾ The Cr-Ti-Si coating is 3 to 4 mils thick.

Oxidation life of the coating on unalloyed columbium, FS82, Cb752, D43, D31, D36, and B66 alloys in cyclic furnace oxidation tests is given in Figure 1 and Table 1. The coating generally was protective for greater than 150 hours at temperatures up to 2500 F, except for the shorter lives exhibited at low temperatures by specimens that were not precoated with titanium. Note that the titanium precoat increased coating life on even the titanium-bearing alloys (D31 and D36) at low temperatures. Coating life dropped sharply at 2800 F, but it still afforded 1 to 4 hours' protection to B66 alloy at 3000 F.

The coating system also has been oxidation tested at reduced pressures to ascertain its propensity for failure under the conditions of high temperature and low pressure encountered during re-entry.⁽³⁾ Coated D14 specimens were exposed in the static

*References are given on page 89.

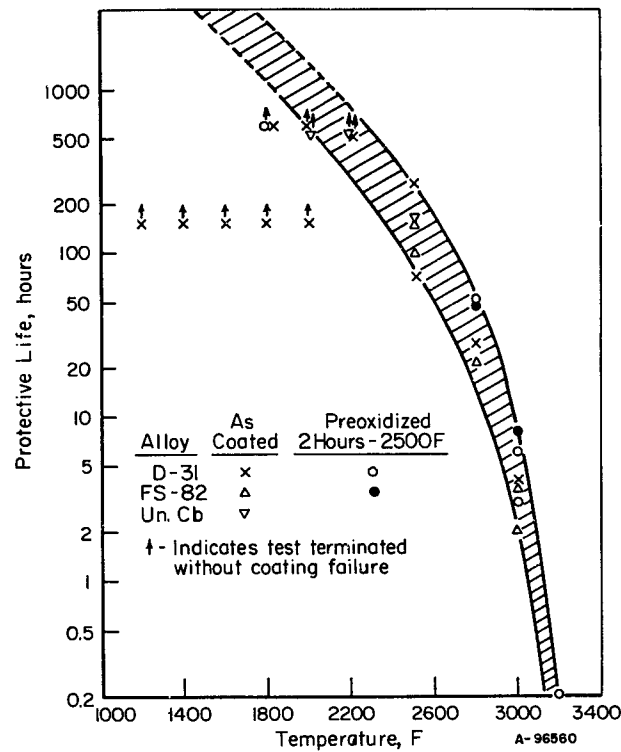


FIGURE 1. PROTECTIVE LIFE OF Cr-Ti-Si COATING IN CYCLIC FURNACE OXIDATION TESTS⁽¹⁾

TABLE 1. OXIDATION LIFE OF Cr-Ti-Si COATING ON COLUMBIUM ALLOYS IN STILL AIR^{(a)(1)}

Alloy	Alloy Composition	Protective Life, hours, at Indicated Temperature							
		1200 F	1800 F	2000 F	2300 F	2500 F	2600 F	2800 F	3000 F
Cb752	Cb-10W-4Zr ^(b)	>150	>150	92 to >150	>150	>150	--	--	--
D43	Cb-10W-1Zr	>150	>150	>150	>150	>150	--	--	--
D14	Cb-5Zr	>150	85 to >150	>150	>150	>150	--	--	--
D31	Cb-10Ti-10Mo	>150	>150	>150	>150	>150	--	--	--
D31 ^(c)	Cb-10Ti-10Mo	24	53	92 to >150	>150	>150	--	--	--
D36	Cb-10Ti-5Zr	>150	>150	>150	>150	>150	--	--	--
D36 ^(c)	Cb-10Ti-5Zr	24	53	92-150	>150	>150	--	--	--
B66	Cb-5Mo-5V-1Zr	>150	>150	>150	>150	>150	>100	3-9	1-4 ^(d)

(a) Cycling procedure: Up to 2600 F - once each hour for 8 hours, then a 16-hour cycle in each 24-hour period.
 2800 F - approximately once each 0.5 hour.
 3000 F - approximately once each 0.3 hour.

Specimens were sheet materials, 30 to 60 mils thick. Values are range of oxidation lives for four specimens.

(b) Obsolete composition. Cb752 is now Cb-10W-2.5Zr.

(c) Not precoated with titanium; all others precoated.

(d) Preoxidized 2 hours in air at 2500 F.

atmosphere of a vacuum furnace under air pressures of 10^{-2} , 1, or 5 mm at 2500 F for times ranging up to 4 hours. The coating lost about $6 \text{ mg/cm}^2/\text{hour}$ during the exposure at 10^{-2} mm pressure. Microstructural changes and a green deposit on the retort walls which accompanied the weight loss has led TRW to conclude that chromium evaporated from the coating. The results of the subsequent oxidation tests at 2500 F under atmospheric air pressure are presented in Table 2. The low-pressure pre-exposure did not impair the oxidation resistance of the coating at 1800 F, but it did reduce coating life at 2500 F, especially after the pre-exposure treatment of 4 hours at 10^{-2} mm pressure. The outer coating region which underwent microstructural changes during the vacuum treatment oxidized rapidly during the atmospheric-pressure oxidation exposure. Future tests are planned to elucidate the oxidation characteristics of the coating over a range of pressures and temperatures.

TABLE 2. PROTECTIVENESS OF Cr-Ti-Si COATING ON D14 ALLOY AT ATMOSPHERIC PRESSURE AFTER PRE-EXPOSURE AT REDUCED PRESSURE⁽³⁾

Pre-Exposure at 2500 F at Reduced Pressure		Subsequent Oxidation Life of Coating at 1 Atmosphere Air Pressure	
Air Pressure, mm	Time, hr	1800 F	2500 F
No pre-exposure		>200, >200	>104, >104
10^{-2}	1	>200, >200	63
10^{-2}	2	>200, >200	81
10^{-2}	4	>200, >200	6
1	1	>24(a)	>24(a)
5	1	>24(a)	>24(a)

(a) Postoxidation test not completed.

Recrystallized 0.032-inch thick, B66 alloy sheet coated with Cr-Ti-Si has been evaluated in several tests by TRW. Thermal-shock and erosion-test specimens were 1 by 2 by 0.032-inch sheet bent over a 3/16-inch radius before coating. Specimens were tested in three conditions:

- (1) As coated
- (2) Preoxidized 24 hours at 1800 F
- (3) Preoxidized 24 hours at 2500 F.

The test consisted of heating the convex surface with an oxidizing oxyacetylene flame to 2500 F at an average rate of 100 F/sec, followed immediately by cooling with an air jet at the rate of 200 F/sec. The coated specimens were unfailed after 250 such thermal cycles.

B66 specimens were bend tested (4T radius) to ascertain the effects of the coating thermal treatment, the coating, and subsequent oxidation exposure on the ductile-to-brittle transition temperature. The bend-test results are shown in Figure 2. The coating and subsequent thermal exposures in argon or air at 1800 or 2500 F increased the transition temperature by from 300 to 550 F.

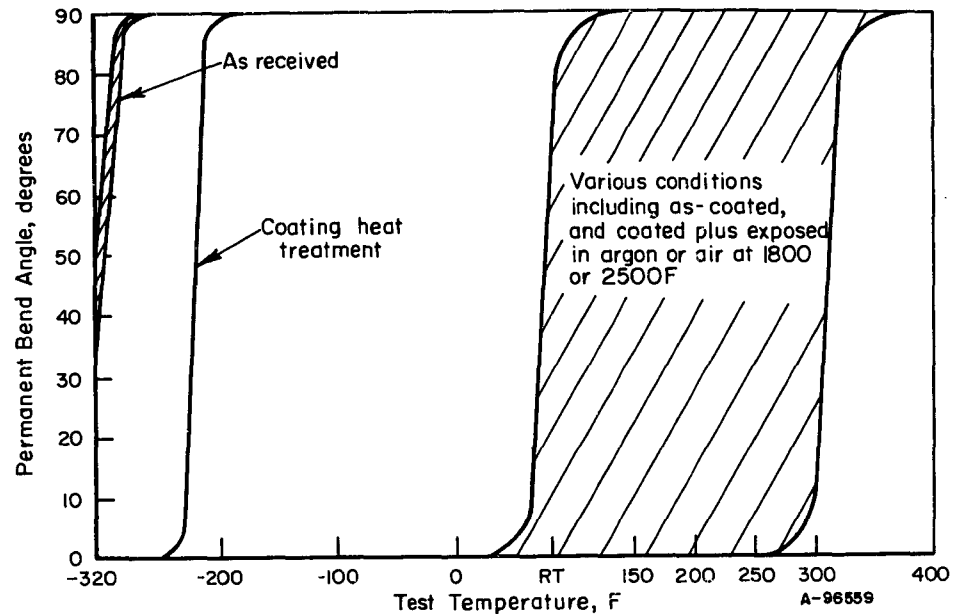


FIGURE 2. BEND TRANSITION TEMPERATURES OF UNCOATED AND Cr-Ti-Si-COATED B66 ALLOY AFTER VARIOUS HEAT TREATMENTS AND CYCLIC OXIDATION EXPOSURES⁽¹⁾

The coated B66 alloy sheet was also tensile tested. As-coated specimens exhibited only 3 per cent elongation (in 1 inch) at room temperature, so the balance of the tests were conducted at 200 F to compare tensile properties of heat-treated specimens with ductile as-coated specimens. The prior histories of the tensile specimens are given below:

Bare Substrate

- (1) As-received, recrystallized condition.
- (2) Subjected to coating thermal treatment.

Coated Substrate

- (1) As coated.
- (2) Oxidized 100 hours in still air at 1800 F while under tensile stresses of 10, 20, and 40 per cent of yield strength. Creep was 0, 0.1, and 0.7 per cent, respectively.
- (3) Heated in argon for 100 hours at 1800 F.
- (4) Oxidized in still air at 2500 F while under tensile stress: (a) 24 hours, 10 per cent of yield strength and (b) 8 hours, 20 per cent of yield strength. Creep ranged from 4 to 7 per cent.

(5) Heat treated in argon for 8 and 24 hours at 2500 F.

These thermal and stress treatments had only slight effects on the tensile properties at 200 F, as indicated below:

	<u>Bare Substrate</u>	<u>All Coated Conditions</u>
Tensile Strength	93,000 psi	80,000-90,000 psi
Yield Strength	67,000 psi	56,000-66,000 psi
Elongation in 1 Inch	28 per cent	20-26 per cent

The various treatments lowered the ductility slightly at 200 F. Because the original sheet thickness was used to calculate the cross-sectional areas for all strength values, no real variation in either tensile or yield strengths of the substrate at 200 F is apparent. The creep (up to 7 per cent permanent deformation) that occurred during the stress-oxidation treatments did not impair the oxidation resistance of the coating. These tests indicate that the ductile-to-brittle transition temperature in tension was below 200 F for all conditions tested.

Figure 3 is a stress-rupture plot for Cr-Ti-Si-coated FS82 (Cb-33Ta-1Zr) sheet tested in air at 2500 F⁽⁴⁾. Coated FS82 exhibits about the same rupture strength as bare FS82.

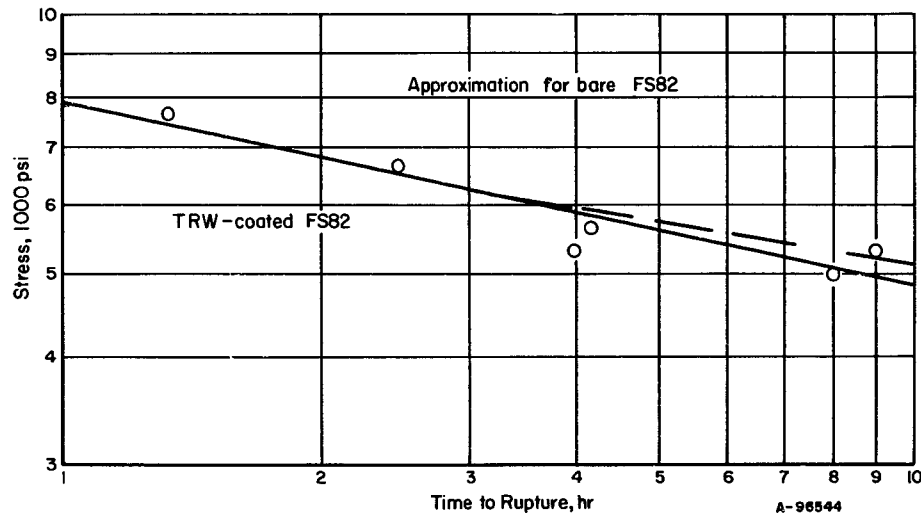


FIGURE 3. 2500 F STRESS-RUPTURE STRENGTH OF 20-MIL FS82 SHEET COATED WITH TAPCO Ti-Cr-Si COATING TESTED IN AIR⁽⁴⁾

Boeing Straight Silicide and Si-(SiC + SiO₂) Coatings

Boeing has done extensive work on applying and testing straight silicide coatings, sometimes referred to as Disil coatings, and an improved-emittance silicide coating on

FS82 (Cb-33Ta-1Zr) and D36 (Cb-10Ti-5Zr) alloys.⁽⁵⁾ The coatings also have been applied to other alloys. The straight silicide coatings, usually about 1.5 mils thick, are applied by the fluidized-bed process, which has been described elsewhere^(5,6), at temperatures below 2000 F. The emittance-improved coating, designated Si-(SiC + SiO₂) is produced by applying an overlay of silicon carbide dispersed in silicon dioxide sol on a straight silicide coating and firing at 2000 F.

Results of oxyacetylene torch tests of the straight silicide coating on sheet specimens 12 to 50 mils thick and 2 inches square are shown in Figure 4. Maximum temperature variation of the sheet specimen was 500 F from the 3/4-inch hot zone to the edges. The minimum protective life of the coating on D36 was 4 hours at 2700 F and 2.5 hours at 3000 F (uncorrected optical temperatures), whereas it was only 1.5 and 1 hours on FS82 at the respective temperatures.

Emittance of the straight silicide coating is shown in Figure 5. The higher emittance of coated D36 relative to FS82 has been attributed to the influence of the titanium in D36⁽⁷⁾. Emittance has been increased further with the Si-(SiC + SiO₂) coating on D36 to values between 0.80 and 0.96 under the conditions of temperature and ambient air pressure encountered in a typical Dyna-Soar re-entry profile.⁽⁵⁾

Vought II and Vought IV Modified Silicide Coatings⁽⁸⁾

Chance Vought has optimized the pack-cementation process parameters for applying its Vought II (Si-Cr-Al) and Vought IV (Si-Cr-B) coatings on columbium alloys, as described below:

First Cycle - Siliconizing

Pack composition: 60 per cent Si, 6 to 10 per cent halide, balance
325-mesh Al₂O₃

Furnacing: 16 hours, 2100 F

Second Cycle for Vought II - Codeposition of Cr + Al

Pack composition: 35 per cent Cr, 20 per cent Al, 4 per cent halide,
balance 325-mesh Al₂O₃

Furnacing: 16 hours, 2300 F

Second Cycle for Vought IV - Codeposition of Cr + B

Pack composition: 30 per cent Cr, 30 per cent ferroboron, 4 per cent
halide, balance 325-mesh Al₂O₃

Furnacing: 16 hours, 2200 F

The inner region of coatings applied in this manner is CbSi₂ while the outer coating region contains a variety of phases, which have been identified by X-ray techniques as:

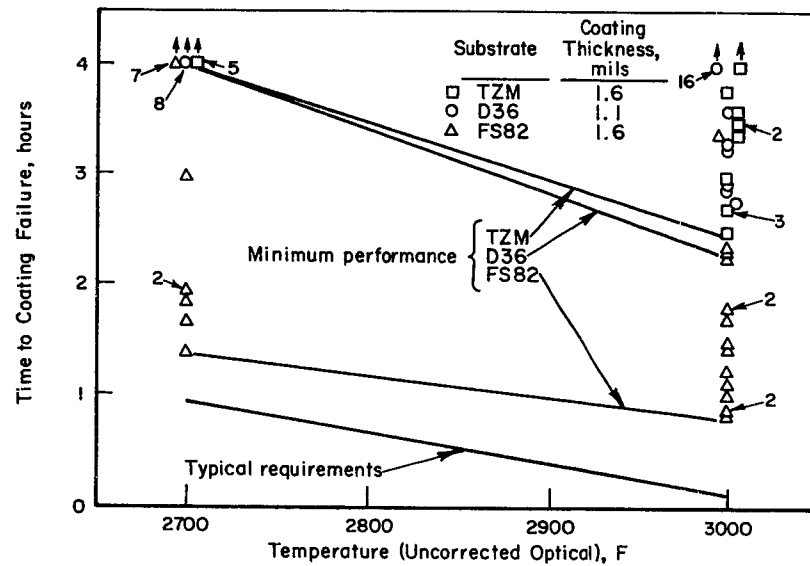


FIGURE 4. OXIDATION LIFE OF BOEING'S STRAIGHT SILICIDE COATING ON D36, FS82, AND TZM IN OXYACETYLENE TORCH TESTS(5)

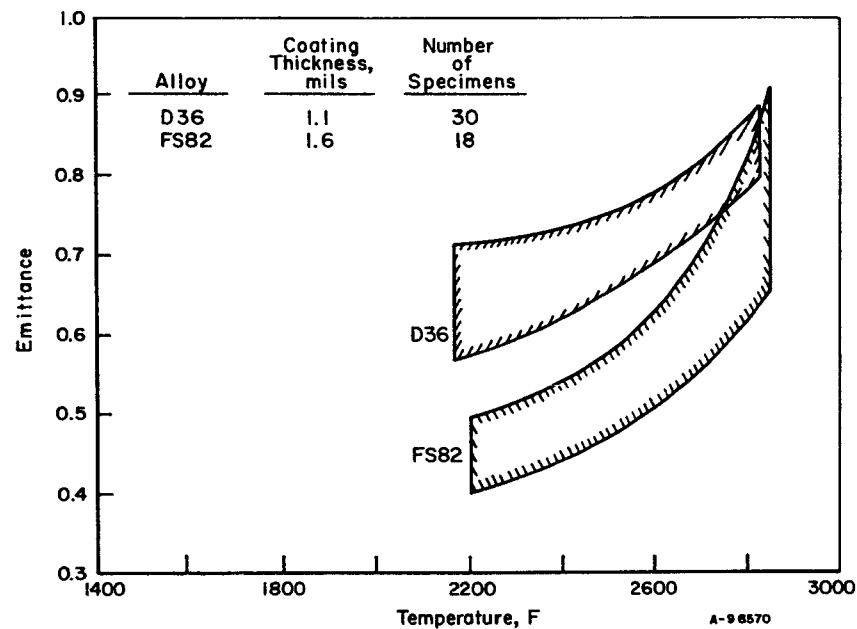


FIGURE 5. EMITTANCE OF BOEING'S STRAIGHT SILICIDE COATING ON D36 AND FS82 ALLOYS(5)

- (1) In Vought II coating - CbAl_3 , CbCr_2 , Cr_3Si , Al_5Cr , and CbSi_2
- (2) In Vought IV coating - CrB , FeB , CbCr_2 , Cr_3Si , CbB_2 , and CbSi_2 .

These coatings are typically about 2 mils thick.

Oxidation resistance of the two coatings on Cb-1Zr, D31, and C103 (Cb-10Hf-1Ti) alloys is given in Table 3. In cyclic furnace tests at 2600 F, average coating life was 9 to 12 hours, with Vought IV exhibiting slightly better performance. Propensity for low-temperature pest failure was investigated by exposing specimens successively for 1 hour at 2400, 1000, 1200, 1400, 1600, 1800, 2000, and 2400 F. The Vought IV coating displayed superior resistance to failure in this test (Table 3).

TABLE 3. OXIDATION RESISTANCE OF VUGHT COATINGS ON 20-MIL COLUMBIUM ALLOY SHEET⁽⁸⁾

Alloy	Coating	2600 F Test Results ^(a)	
		Time to Coating Failure, hr	
		Minimum - Maximum	Average
		(3 specimens)	
Cb-1Zr	Vought II	7-12	8.8
Cb-1Zr	Vought IV	9-14	11.2
C103	Vought II	7-13	9.0
C103	Vought IV	8-15	11.4
D31	Vought II	8-12	10.9
D31	Vought IV	8-15	11.5

Alloy	Coating	Low-Temperature Oxidation-Test Results ^(b)
		Failure Temperatures, F ^(c)
Cb-1Zr	Vought II	1400
Cb-1Zr	Vought IV	Full cycle (5), 1600 (1)
C103	Vought II	1400 (5), 2000 (1)
C103	Vought IV	Full cycle (5), 1800 (1)
D31	Vought II	1800 (4), 2000 (1), 1600 (1)
D31	Vought IV	Full cycle

(a) Specimens exposed in air furnace; cooled to room temperature once each hour.

(b) Test consisted of successive 1-hour exposures in a furnace at the following temperatures: 2400, 1000, 1200, 1400, 1600, 1800, 2000, and 2400 F. Specimens were cooled to room temperature after exposure at each temperature.

(c) Failure temperatures for six specimens are given, if they are different. Full cycle means specimen survived entire test without failure of the coating.

Coated bend specimens were bent at room temperature in 0.5 per cent strain increments (outer fiber strain) and oxidized 1 hour in air at 2000 F after each straining increment to determine the resistance of the coatings to oxidation failure after straining. On the Cb-1Zr and C103 alloys, the Vought IV coating withstood 2 per cent deformation and Vought II 1 per cent without loss of short-time oxidation protection. The as-coated D31 specimens (both coatings) fractured after only 0.7 to 1.4 per cent elongation, indicating severe embrittlement due to the coating or the coating process.

Figure 6 shows that the spectral emittance ($\lambda = 0.65$ micron) of the Vought IV coating on unalloyed columbium in vacuum is greater than 0.9 at temperatures up to 2500 F⁽⁹⁾.

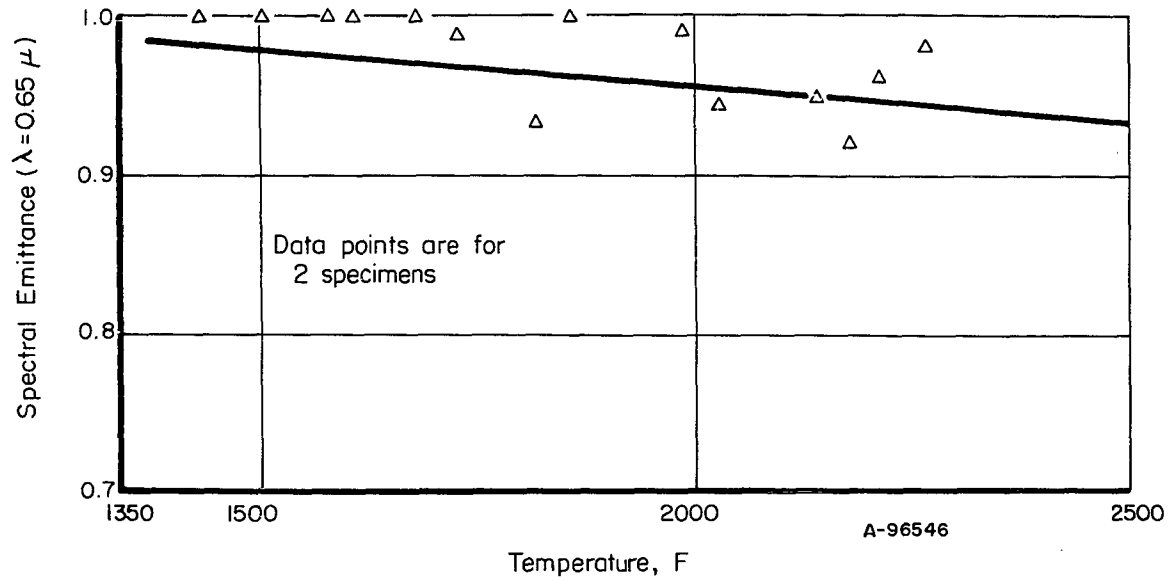


FIGURE 6. SPECTRAL EMITTANCE OF VOUGHT IV COATING ON COLUMBIUM MEASURED IN VACUUM⁽⁹⁾

Pfudler Modified Silicide Coatings

Pfudler has a series of proprietary modified silicide coatings for columbium alloys that are applied by the pack-cementation process.⁽¹⁰⁾ In the first cycle, a layer of chromium alloy is formed. Silicon and other modifying elements are deposited during a second coating cycle. The thickness of coatings applied usually are from 1.5 to 2 mils. Typical coating lives over various substrates in an oxyacetylene torch test are given in Table 4. At 2600 F, where all the coating-substrate systems were tested, the coatings exhibited the longest oxidation lives on D31 alloy (Cb-10Ti-10Mo).

The oxidation performance of Pfudler's PFR-1M and PFR-2M coatings on sheet coupons of Cb-1Zr and F48 also has been investigated by McDonnell.⁽¹¹⁾ The specimens were heated in air with oxyacetylene and plasma arc torches. As shown in Table 5, the coatings were protective for at least 10 to 15 minutes at 3000 F and 5 minutes at 3200 F.

TABLE 4. OXIDATION LIVES OF PFAUDLER MODIFIED SILICIDE COATINGS ON COLUMBIUM ALLOYS IN OXYACETYLENE TORCH TEST⁽¹⁰⁾

Substrate	Coating	Oxidation Life, hours, at Indicated Temperatures		
		2600 F	2800 F	3000 F
Cb	PFR-2M	3-6		0.5-1
D31	PFR-3A	5-28		
D31	PFR-4A	2-14		
D31	PFR-1	5-14		
D31	PFR-1M	16-26	5-11	2-4
FS82	PFR-1M	2-6		0.5-0.8
Cb-1Zr	PFR-1M	3-4	1-4	0.5-4
C103	PFR-2M	>3	0.5-1	
F48	PFR-2M			0.3-1

TABLE 5. TORCH-OXIDATION TESTS OF PFAUDLER PFR-1M AND PFR-2M COATINGS ON COLUMBIUM ALLOYS⁽¹¹⁾

Substrate	Coating	Type of Torch	Test Temperature, F	Test Time, minutes	Coating Performance
Cb-1Zr	PFR-1M	Oxyacetylene	2800	15	No coating failure
Cb-1Zr	PFR-1M	Oxyacetylene	3000	15	Edge failure at 10 minutes
Cb-1Zr	PFR-1M	Oxyacetylene	3000	15	No coating failure
Cb-1Zr	PFR-1M	Oxyacetylene	3200	5	No coating failure
Cb-1Zr	PFR-1M	Plasma arc	3000	5	No coating failure
F48	PFR-2M	Oxyacetylene	3000	15	No coating failure

LB-2 Aluminide Coating

The LB-2 aluminide coating, originally developed by General Electric Corporation in conjunction with McDonnell Aircraft Company, now is being used extensively by McDonnell to coat columbium alloy components of the ASSET vehicle. The coating is applied by the slurry process* using a slurry of Al-10Cr-2Si alloy powder suspended in a mixture of several organic vehicles. The coating is dried in air at 150 F and a second coat is similarly applied. The "green" coating is diffusion annealed at 1700 to 1900 F in argon to form primarily CbAl_3 .⁽¹²⁾ The resulting coating is 2 to 5 mils thick. (McDonnell has observed that using the Al-10Cr-2Si alloy powder for the second coat instead of unalloyed aluminum, as was the practice in earlier work⁽¹³⁾, improves the coating's oxidation performance of low temperatures without degrading performance at high temperatures.) The LB-2 coating is normally protective for a minimum of 2 hours at 2500 F or 1/2 hour at 2700 F at atmospheric pressure.⁽¹⁴⁾

McDonnell has tensile tested 36-mil Cb-5Zr sheet coated with LB-2 at room temperature after short postcoating exposures in argon or air at 1900 F.⁽¹⁵⁾ The purpose was to investigate the effects of an "oxidation proof test" on the tensile properties of the substrate by isolating the effects of temperature and oxidation. The tensile test results for bare and coated specimens are given in Table 6. The coating and subsequent thermal treatments for up to 4 hours in argon or air had little effect on the tensile properties of the Cb-5Zr sheet. The maximum decrease in room-temperature yield and tensile strength and elongation was 10 per cent; the reduction in strength might be expected since the reported strength values are based on the original sheet thickness.

TABLE 6. ROOM-TEMPERATURE TENSILE PROPERTIES^(a) OF 36-MIL Cb-5Zr SHEET COATED WITH LB-2⁽¹⁵⁾

Thermal Treatment of Coated Test Specimens	Yield Strength, psi	Ultimate Strength, psi	Elongation in 1 Inch, per cent
Uncoated sheet	51,000-53,000	67,000-68,000	24-26
1 hr, 1900 F, in argon	47,000-49,000	64,000-65,000	20-22
2 hr, 1900 F, in argon	49,000-51,000	62,000-65,000	24-27
4 hr, 1900 F, in argon	47,000-48,000	64,000	22-23
2 hr, 1900 F, in argon; plus 1/2 hr at 1900 F in air	53,000-54,000	64,000-67,000	19-24

(a) Range of values obtained with three specimens is reported. Strength values are based on original sheet thickness.

Table 7 presents some room-temperature tensile-test data for LB-2-coated FS82 alloy. The yield and tensile strength in the as-coated condition and after oxidation exposure at 2500 F were midway between that for stress-relieved and recrystallized bare FS82 (recrystallization temperature is between 2100 and 2400 F). Elongation increased to the level of recrystallized material during the oxidation exposures.

*Slurry processes comprise application of the active coating material in powder form suspended in a vehicle, by brushing, dipping, or spraying.

TABLE 7. ROOM-TEMPERATURE TENSILE PROPERTIES OF FS82 COLUMBIUM ALLOY COATED WITH LB-2⁽¹⁶⁾

Condition of Test Specimen	Room-Temperature Strength, 1000 psi		Elongation in 2 Inches, per cent
	Ultimate	0.2% Yield	
As coated	65	45	17
Oxidized 1 hr at 1800 F + 1.5 hr at 2540 F	64	49	22
Oxidized 2 hr at 2500 F	63	49	27
Bare stress-relieved sheet	80	70	11
Bare recrystallized sheet	55	37	25

General Telephone and Electronics Tin-Aluminum Coating

General Telephone and Electronics has developed a family of tin-aluminum coatings applied by the slurry process. Although developed originally for tantalum alloys, their (Sn-25Al)-10TaAl₃ coating composition also protects columbium.⁽¹⁷⁾ The coating system and process are described in the section on coatings for tantalum.

The oxidation-performance data of the (Sn-25Al)-10TaAl₃ coating on Cb-5Zr alloy are given in Table 8. The coating protected the substrate for about 90 hours at 1400 and 2000 F, 40 hours at 2200 F, and 20 hours at 2400 F. Oxidation life increased with coating thickness which depended on the number of coating layers applied. Coating thickness was more than doubled by applying a second layer of the coating. In general, coatings ranged from about 1 to 4 mils thick.

TABLE 8. OXIDATION LIFE OF (Sn-25Al)-10TaAl₃ COATING ON 20-MIL Cb-5Zr ALLOY SHEET^{(a)(17)}

Oxidation Temperature, F	Number of Coats Applied	Weight Gain During Coating, mg/cm ² ^(b)	Oxidation Life, hr	
			Range	Average
1400	1	16-28	5-17	9
1400	2	44-54	40-100	88
2000	2	42-50	75-100	95
2200	1	19-36	9-19	14
2200	2	43-55	18-54	45
2400	1	18-32	1-6	4
2400	2	43-55	14-27	21

(a) Tests conducted in still air in a furnace. Specimens generally cycled to room temperature ten times each 24 hours.

Tensile and creep properties of Cb-5Zr sheet coated with the (Sn-25Al)-10TaAl₃ system are given in Table 9 and Figure 7. Strength values were calculated using the original thickness of the sheet. Yield, tensile, and stress-rupture strengths of coated specimens were only slightly lower than those of bare Cb-5Zr sheet, in accord with the reduction of sheet thickness effected by the coating. Tensile elongation compared favorably with that for bare substrate, except at 2400 F where the excessive plastic deformation may have triggered a coating failure and attendant failure of the specimen.

NAA-85 Aluminide Coating

North American Aviation has developed an aluminide coating, designated NAA-85, primarily for columbium alloys.^(6,18) It is applied by the slurry process using a slurry consisting of aluminum and unidentified ceramic powders in an organic vehicle. The "green" coating is diffusion annealed for 1 hour at 1900 F in argon during which the aluminum reacts with the substrate to form columbium aluminides.

The coating is capable of protecting FS82 alloy from oxidation for 5 hours at 2600 F in static air.⁽¹⁸⁾ No pest-failure problem has been encountered by North American in oxidation tests at temperatures ranging from 1800 to 2600 F. Low-pressure testing has indicated that NAA-85 remains protective on Cb752 and C129 alloys for more than 15 minutes at 2250 F in air at 10⁻⁵ mm of mercury⁽¹⁸⁾.

The total normal emittance of the coating on FS82 alloy is tabulated below:⁽¹⁸⁾

Temperature, F	Emittance
1000	0.90
1500	0.88
1850	0.85
2300	0.80

The tensile properties at 2600 F of FS82 coated with NAA-85 are given in Table 10. The structure of the FS82 sheet when it was tested at 2600 F is not known. The low tensile strength of coated specimens versus the strengths reported for uncoated sheet (16,000 versus 23,000 psi) could be rationalized by assuming that the coated substrate was completely recrystallized whereas the 30-second heat-up time for the bare substrate allowed only partial recrystallization. Some 2600 F creep data for FS82 coated with NAA-85 are presented in Figure 8.

Other Coatings

There are a few coatings for columbium for which little or no information has been published by the coating developer, but which have been tested in the various comparative evaluation programs presented in the next section. These coatings include:

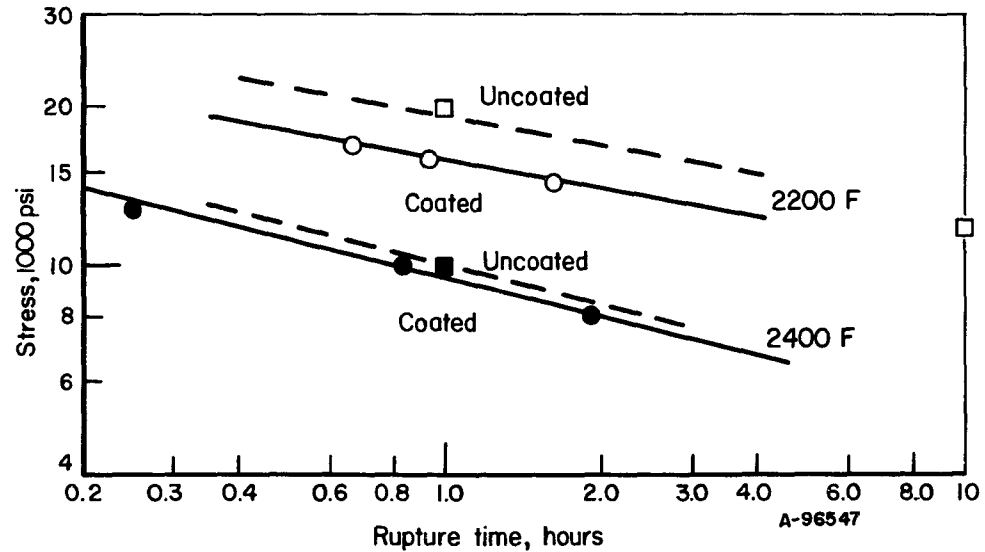
Chromalloy W-2 - pack-cementation silicide developed for molybdenum

Chromizing Durak Cb } pack cementation,
Durak KP } modified silicides

TABLE 9. TENSILE PROPERTIES OF 20-MIL Cb-5Zr SHEET COATED WITH (Sn-25Al)-10TaAl₃ AND TESTED IN AIR⁽¹⁷⁾

Condition of Test Specimen	Test Temperature, F	Yield Strength ^(a) , psi	Tensile Strength ^(a) , psi	Elongation, per cent	Gage Length, in.
<u>Coated Specimens</u>					
As coated	RT	53,000	69,000	23	2
As coated	2000	31,000	39,000	21	1
As coated	2200	20,000	28,000	31	1
As coated	2400	15,000	19,000	47	1
Coated + oxidized 1 hour at 2000 F	RT	44,000	60,000	19	1
Coated + oxidized 1 hour at 2400 F	RT	27,000	50,000	24	1
<u>Typical Properties for Uncoated Stress-Relieved Cb-5Zr Sheet</u>					
Uncoated	RT	61,000	75,000	15	--
Uncoated	2000	28,000	40,000	32	--
Uncoated	2400	12,000	17,000	90	--

(a) Strengths of coated specimens based on substrate thickness prior to application of coating.

FIGURE 7. STRESS-RUPTURE PROPERTIES FOR 20-MIL Cb-5Zr COATED WITH (Sn-25Al)-10TaAl₃ AND TESTED IN AIR⁽¹⁷⁾

Note: uncoated specimens tested in argon.

TABLE 10. 2600 F TENSILE PROPERTIES OF FS82 COLUMBIUM ALLOY
COATED WITH NAA-85⁽¹⁹⁾

Ultimate Tensile Strength, psi	0.2% Offset Yield Strength, psi	Elongation in 2 Inches, per cent
12,700	7,900	25
15,800 ^(a)	12,300	20
15,500 ^(a)	10,900	21
17,700 ^(a)	15,300	18
17,600	13,100	27
16,500	--	17
23,000 ^(b)	13,000 ^(b)	--

(a) After 1 per cent strain for creep test at 2600 F.

(b) Uncoated sheet data for comparison. Heat-up time to test temperature was 30 seconds.

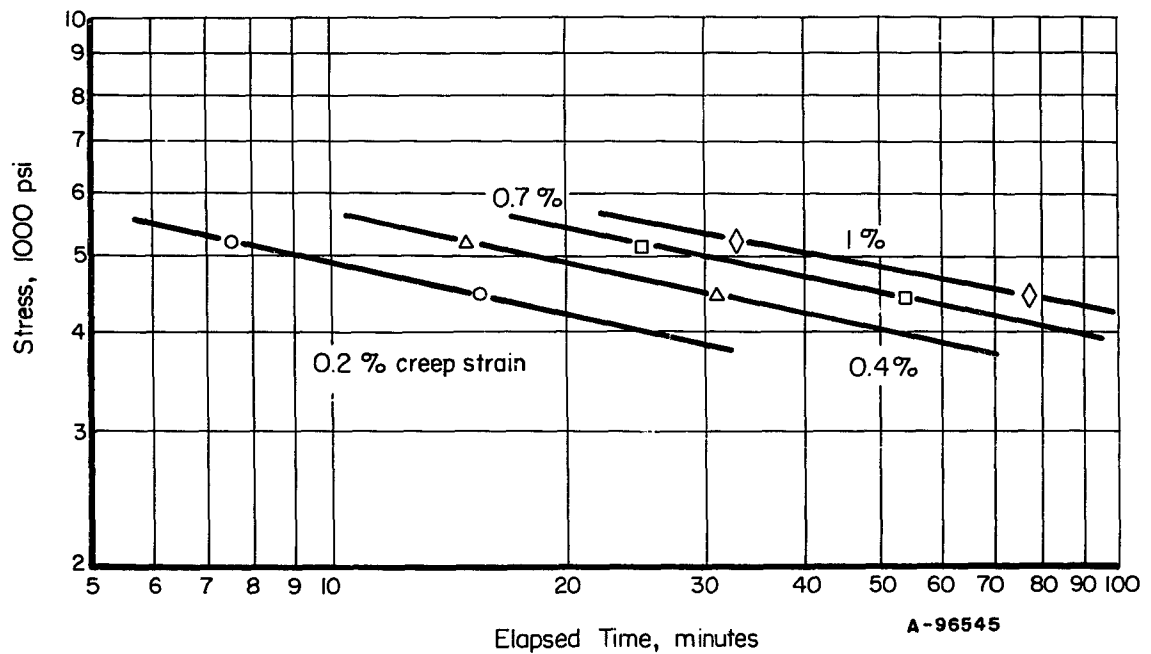


FIGURE 8. CREEP STRAIN AT 2600 F OF FS82 ALLOY COATED WITH
NAA-85 ALUMINIDE COATING⁽¹⁹⁾

General Technology Corp. - pack cementation, modified silicide

General Telephone and Electronics - pack titanizing, followed by either:

- (a) Hot dip in Al-Cr-Si bath, or
- (b) Pack siliconizing.

Pratt & Whitney, CANEL - pack cementation, modified silicide.

Comparative Evaluations of Coatings

Comparative Evaluation of Coatings on Columbium, D31 and F48 Alloys(20)

In 1961 Thompson Ramo Wooldridge (TRW) conducted a comparative evaluation of several of the more promising coating systems for columbium alloys. The substrates coated were 60-mil sheet of unalloyed columbium, D31 (Cb-10Ti-10Mo) and F48 (Cb-15W-5Mo-1Zr) alloys. These are representative low-, medium- and high-strength columbium-base materials, respectively. Test specimens were coated by Sylcor (a subsidiary of GT&E), General Electric, Vought, Chromalloy, TRW, and Chromizing; the coatings are described in Table 11. Coated specimens were evaluated by oxidation, bend, and tension tests.

The protectiveness of the coating systems in cyclic furnace oxidation tests at 2300 and 2500 F is illustrated on Figures 9 and 10. The TRW coating exhibited superior oxidation life; it was protective for greater than 300 hours at 2300 F and for about 200 hours at 2500 F. The Sylcor and GE coatings lasted for up to 300 hours at 2300 F and 20 hours at 2500 F. The thickest coatings (i. e., Sylcor, GE, and TRW) provided the longest oxidation lives at 2300 F. In general, the coatings exhibited greater than average life on the titanium-bearing D31 alloy and less than average life on unalloyed columbium.

The ductile-to-brittle bend transition temperatures of the coated substrates were estimated by bend testing three specimens over a 1.5T bend radius at various temperatures. Figures 11 and 12 show the bend transition temperatures of the coated D31 and F48 alloys in the following conditions:

- (1) As coated
- (2) Coated and oxidized 2 hours at 2500 F
- (3) Coated and heat treated in vacuum for 2 hours at 2500 F.

The transition temperatures for coated columbium specimens in these three conditions were below room temperature with one exception; the Chromizing coating embrittled columbium in the as-coated condition, but not after either of the thermal treatments. As can be seen in Figure 11, the coatings applied to D31 alloy by Chromalloy, Chromizing, and TRW resulted in the largest increase in transition temperature in the as-coated condition. The Vought coating was moderately detrimental, and the degradation of

TABLE 11. COATING SYSTEMS EVALUATED BY THOMPSON RAMO WOOLDRIDGE
ON UNALLOYED COLUMBIUM, D31, AND F48 ALLOYS⁽²⁰⁾

Organization That Applied Coating	Coating	Average Coating Thickness, mils	Coating Process
Sylcor ^(a)	--	5	F48 and columbium were titanized in titanium sponge in a vacuum, then hot dipped in Al-Cr-Si bath; D31 was only hot dipped in Al-Cr-Ti bath; all specimens diffusion annealed 1 hour at 1900 F in argon
General Electric	LB-2	8	Two-layer paint-and-sinter coating; Al-Cr-Si layer painted on followed by unalloyed Al top coat; sintered at 1900 F under argon
Vought	--	2	Two 16-hour pack-cementation cycles at 1900 F followed by preoxidation consisting of 32 hours at 1900 F
Chromalloy	W-2	1.8	Chromium modified silicide coating applied by pack cementation
TRW	Cr-Ti-Si	3.7	Three-cycle vacuum pack cementation: (1) Titanized in KF-activated Ti pack, 8 hours at 2100 F (2) Cr-Ti deposited in KF-activated 50Cr-50Ti pack, 8 hours at 2300 F (3) Siliconized 5 hours at 2150 F
Chromizing	Durak Cb	1.5	Unspecified; believed to be a pack-cementation silicide coating, perhaps modified with boron

(a) A subsidiary of General Telephone and Electronics.

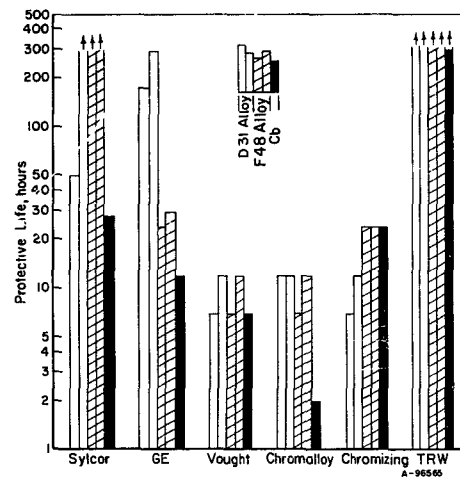


FIGURE 9. PROTECTIVE LIFE OF COATINGS ON COLUMBIUM, D31, AND F48 ALLOYS IN OXIDATION TESTS IN STILL AIR AT 2300 F⁽²⁰⁾

Specimens cycled to room temperature each hour for 24 hours; thereafter cycled nine times each 24-hour period. Each bar represents one test specimen.

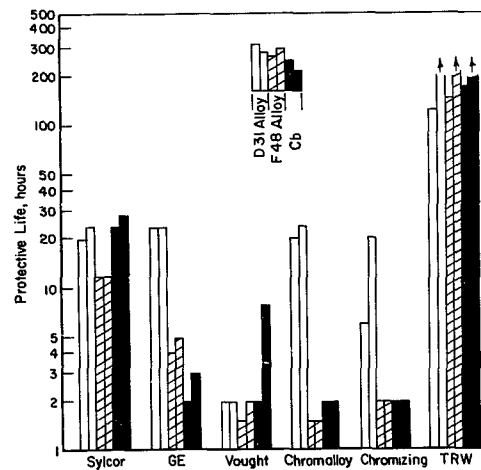


FIGURE 10. PROTECTIVE LIFE OF COATINGS ON COLUMBIUM, D31, AND F48 ALLOYS IN OXIDATION TESTS IN STILL AIR AT 2500 F⁽²⁰⁾

Specimens cycled to room temperature once each hour for 24 hours; thereafter cycled nine times each 24-hour period. Each bar represents one test specimen.

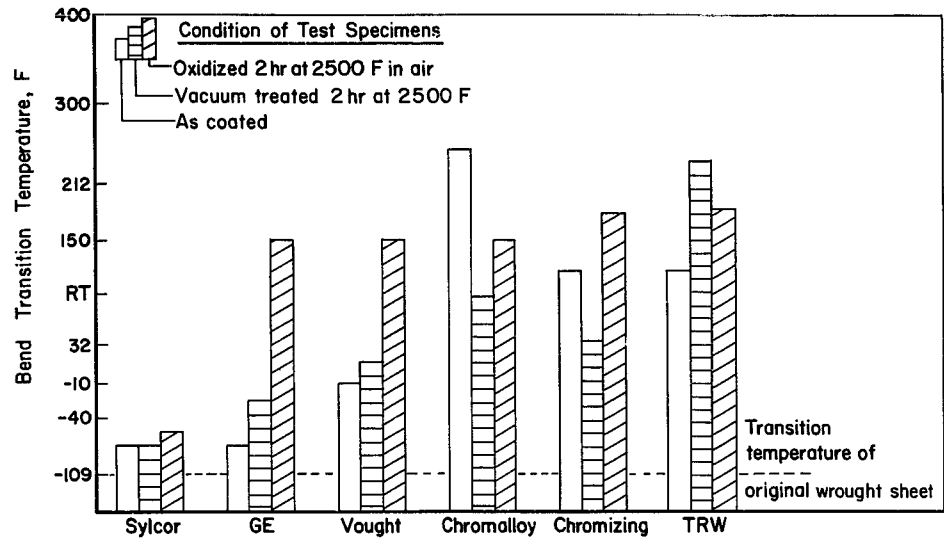


FIGURE 11. BEND TRANSITION TEMPERATURE OF COATED D31 ALLOY(20)

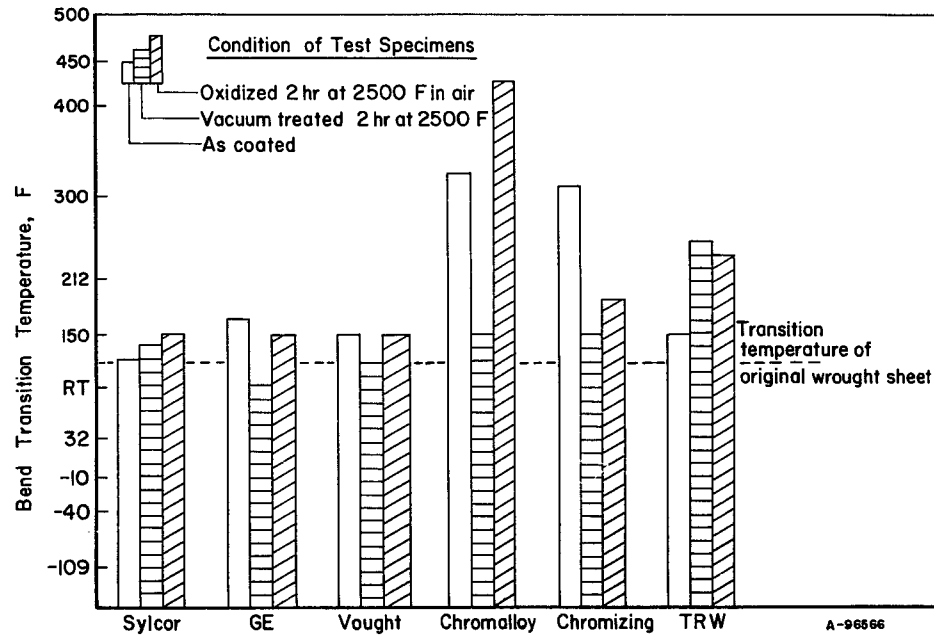


FIGURE 12. BEND TRANSITION TEMPERATURE OF COATED F48 ALLOY(20)

low-temperature ductility by the Sylcor and GE coatings was negligible. Vacuum heat treatment beneficially lowered the transition temperature of Chromalloy- and Chromizing-coated D31, suggesting that degradation in the as-coated condition may have been partially due to interstitial (hydrogen) contamination; for other coatings vacuum treatment had little effect or was detrimental (e. g. , TRW coating). Postcoating oxidation exposures were markedly detrimental to transition behavior of the GE- and Vought-coated D31; other coated systems were affected less by this parameter.

Over F48, only the Chromalloy and Chromizing coatings increased the transition temperature appreciably, and as was true for these coatings over columbium and D31, vacuum heat treatment greatly reduced this degradation. Only the TRW coating exhibited substantial increase in transition temperature as a result of the vacuum treatment. Except for Chromalloy-coated F48, the transition behavior of the various systems was affected little by the oxidation exposure, in contrast to the general behavior of coated D31.

Over all, the Sylcor coating and/or process exhibited the best low-temperature mechanical compatibility with columbium and the two alloys.

Table 12 presents tensile properties for coated specimens which were tested in the following conditions:

- (1) As coated
- (2) Heat treated in vacuum for 2 hours at 2500 F
- (3) Oxidized in furnace for 2 hours at 2500 F while under a tensile stress equal to 20 per cent of the yield strength of the base metal. Specimens underwent 1 to 2 per cent creep.

Unalloyed columbium was tensile tested at room temperature; D31 was tested at room temperature and 1000 F, and F48 was tested at 1000 F. The F48 alloy (and probably the D31 and unalloyed columbium) was in the wrought condition prior to application of the coatings. Some of the coatings were applied within the recrystallization-temperature range of unalloyed columbium (1600 to 2000 F) and D31 alloy (the same or slightly higher temperature range than for columbium), and F48 (2200 to 3000 F), so varying amounts of recrystallization could be expected to occur during coating. The 2500 F vacuum anneal would recrystallize pure columbium and restore the 21,000-psi tensile strength that was characteristic of the recrystallized material. Unalloyed columbium coated by Sylcor, GE, and TRW had about the expected tensile properties in the as-coated condition. The unusually high strength of columbium coated by Vought, Chromalloy, and Chromizing in the as-coated and vacuum-annealed conditions suggests that the substrate was contaminated during the coating process. The Chromizing coating embrittled the columbium, but the Vought and Chromalloy coatings did not. The coated D31 specimens exhibited adequate ductility for design purposes (7 to 18 per cent) with the exception of coatings applied by Chromalloy and TRW which embrittled the substrate at room temperature. Tensile strengths were as expected, assuming that the substrates were mostly recrystallized. (Tensile strength of recrystallized D31 is about 95,000 and 65,000 psi, respectively, at room temperature and 1000 F.) D31 specimens coated by GE had the lowest strength, perhaps due to exceptional diffusion consumption of the substrate. The strengths of F48 specimens reflected the combined effects of retained cold work, substrate consumption, and substrate contamination. Vacuum annealing at 2500 F

TABLE 12. TENSILE-TEST DATA FOR COATED COLUMBIUM, D31, AND F48 ALLOYS⁽²⁰⁾

Coating	As Coated			Vacuum Annealed 2 Hr at 2500 F			Oxidized 2 Hr at 2500 F in Air		
	Tensile Strength, psi	0.2 Per Cent Offset Yield Strength, psi	Elongation in 1 Inch, per cent	Tensile Strength, psi	0.2 Per Cent Offset Yield Strength, psi	Elongation in 1 Inch, per cent	Tensile Strength, psi	0.2 Per Cent Offset Yield Strength, psi	Elongation in 1 Inch, per cent
<u>Unalloyed Columbium, Tensile Tested at Room Temperature^(a)</u>									
Sylcor	19,620	10,750	28.4	20,200	8,670	19.6	19,100	8,460	17.4
GE	22,000	9,260	39.2	21,000	11,800	22.0	(b)	--	--
Vought	47,200	28,900	25.4	33,900	23,700	24.8	32,200	23,500	16.4
Chromalloy	42,800	32,500	28.4	36,800	20,750	25.0	25,500 ^(c)	--	^(c)
Chromizing	43,800	--	0	38,000	37,800	1.6	28,900	28,400	1.8
TRW	25,300	13,500	20.2	20,150	11,660	19.2	23,400	13,700	15.1
<u>D31 Alloy, Tensile Tested at Room Temperature^(d)</u>									
Sylcor	91,600	85,400	20.6	88,000	76,000	22.2	92,000	83,400	18.2
GE	81,400	75,000	19.6	80,000	69,400	21.4	80,400	74,000	14.6
Vought	92,000	82,600	13.8	85,400	73,400	20.6	95,400	86,000	16.4
Chromalloy	(e)	--	--	91,500	78,600	25.6	(e)	--	--
Chromizing	94,000	85,400	10.2	91,500	78,600	10.2	98,000	89,400	8.4
TRW	80,000	--	0	(e)	--	--	(e)	--	--
<u>D31 Alloy, Tensile Tested at 1000 F^(f)</u>									
Sylcor	64,000	49,300	12.6	64,000	40,600	13.0	68,000	48,000	8.0
GE	56,600	42,000	12.6	57,300	36,000	12.7	60,000	43,400	7.3
Vought	68,700	45,200	14.8	65,400	38,000	12.6	67,400	48,600	8.2
Chromalloy	62,600	43,400	14.1	65,400	40,600	13.4	69,400	50,000	9.6
Chromizing	62,000	44,600	13.5	64,000	40,000	13.0	68,000	50,000	9.3
TRW	64,600	43,400	12.6	69,400	43,400	14.0	67,400	44,000	11.0
<u>F48 Alloy, Tensile Tested at 1000 F^(g)</u>									
Sylcor	70,600	66,000	11.0	55,400	40,600	7.9	57,300	40,300	5.8
GE	66,700	63,000	3.2	52,000	38,000	5.9	55,700	48,300	0.14
Vought	70,600	66,000	3.8	55,400	42,000	5.3	62,600	46,300	6.0
Chromalloy	62,600	58,700	1.3	57,900	40,000	8.5	66,000	52,000	2.8
Chromizing	76,700	72,400	2.8	62,600	47,400	9.2	65,300	48,000	4.2
TRW	55,000	44,000	7.2	59,300	40,000	7.3	57,300	41,300	7.4

(a) Tensile strength of bare columbium = 62,000 psi in cold-rolled condition and 21,000 psi in recrystallized condition.

(b) Substrate oxidized too extensively to provide meaningful tensile data. Specimen not tested.

(c) Localized substrate oxidation may have affected tensile properties.

(d) Tensile strength of bare D31 = 105,000 psi in wrought condition and 95,000 psi in recrystallized condition.

(e) Specimen broke at loading-pin hole.

(f) Tensile strength of bare recrystallized D31 at 1000 F = 65,000 psi.

(g) Tensile strength of bare F48 = 100,000 psi in as-rolled condition and 60,000 psi in recrystallized condition. Ductility of F48 is about 10 per cent at 1000 F.

reduced strength from that of the as-coated condition while oxidation exposure increased the strength compared to the vacuum-annealed condition. The ductility of F48 specimens generally was low compared to that for uncoated material at 1000 F, which is about 10 per cent.

Comparative Evaluation of Coatings on
D14 and FS85 Alloys^(3, 21)

Thompson Ramo Wooldridge has conducted a screening evaluation of the seven coatings described in Table 13 on D14 alloy and a design-data study with FS85 alloy coated by Pfaudler and TRW. All available commercial coatings were tested on D14 alloy sheet, a readily available low-strength columbium alloy, to select the best coatings for the more extensive evaluation.

TABLE 13. COATINGS EVALUATED BY THOMPSON RAMO WOOLDRIDGE ON
D14 AND FS85 COLUMBIUM ALLOYS⁽²¹⁾

Coating	Organization That Applied Coating	Description of Coating and Coating Process
W-2	Chromalloy	Modified silicide applied by pack cementation
LB-2	McDonnell	Cr-Si-modified aluminide coating applied by paint-and-sinter technique
--	Pfaudler	Cr-Mo-modified silicide applied by 2-cycle pack cementation at 2050 F
--	Pratt & Whitney - CANEL	Two-cycle pack cementation coating: (Cycle 1) 23 hours at 1800 F in 80 vol % alumina, 15 vol % Si powder, 5 vol % Ti powder, plus some CuCl ₂ activator, under argon; (Cycle 2) 16 hours at 1800 F in Cr power pack, under argon
R-506	General Telephone & Electronics (GT&E)	Two-cycle pack-cementation process consist- ing of titanizing under vacuum followed by siliconizing under argon
Cr-Ti-Si	Thompson Ramo Wooldridge (TRW)	Vacuum pack-cementation process: (Cycle 1) Cr-Ti deposited in 50Cr-50Ti pack in 8 hours at 2300 F using KF activator; (Cycle 2) Si applied over Cr-Ti layer in 4 hours at 2000 F in silicon pack activated with KF; D14 speci- mens were pretitanized at 1900 F as the first of 3 coating cycles.
Vought IV	Chance Vought	Two-cycle pack-cementation process: (Cycle 1) Si applied in 16 hours at 2100 F, (Cycle 2) Cr, B, and Fe codeposited in 16 hours at 2200 F

Screening Tests of Coated D14 Alloy. The performances of the seven coatings on 30-mil D14 alloy sheet were compared in the following screening tests:

- (1) Oxidation
- (2) Bend ductility
- (3) Oxidation exposure following prestraining by bending.

The oxidation data for the coatings tested at temperatures of from 1600 to 2600 F are given in Table 14. The TRW coating afforded the most reproducible and longest oxidation life.

TABLE 14. PROTECTIVE LIFE OF VARIOUS COATINGS ON D14 ALLOY IN CYCLIC FURNACE OXIDATION TESTS⁽²¹⁾

Coating Organization	Protective Life, hours ^(a)			
	1600 F	2000 F	2300 F	2600 F
Chromalloy	4, 150, 150	5, 18, 43	5, 6, 16	1, 1, 9
McDonnell	4, 4, 5	16, 16, 17	5, 5, 16	2, 2, 2
Pfautler	67, 150, 150	5, 66, 69	1, 1, 17	9, 11, 11
Pratt & Whitney	150, 150, 150	17, 39, 44	3, 3, 19	1, 2, 2
GT&E	5, 61, 82	6, 21, 39	43, 62, 150	17, 19, 24
TRW	150, 150, 150	150, 150, 150	150, 150, 150	21, 27, 37
Vought	1, 150, 150	130, 150, 150	17, 18, 18	6, 13, 13

(a) Oxidation exposure terminated at 150 hours at 1600, 2000, and 2300 F. At 1600, 2000, and 2300 F, specimens were cycled to room temperature once each hour during the first 24 hours of testing. Thereafter specimens were cycled nine times in each 24-hour period. Specimens were cycled once each hour at 2600 F until failure.

Coated D14 specimens were bend tested at room temperature in the as-coated condition, after 50 hours' preoxidation at 2000 F, and after 10 hours at 2600 F (unless coatings failed in shorter times). The bend tests followed procedures recommended by the Refractory Metal Sheet Rolling Panel of the Materials Advisory Board⁽²²⁾. The bend radius was 4T. The bend transition temperature of bare D14 in the stress-relieved condition was -320 F. In the as-coated condition, specimens coated by McDonnell, Pfautler, GT & E, and TRW, were ductile (90-degree bend) at room temperature. On the other hand, the coatings applied by Chromalloy, Pratt & Whitney, and Vought, embrittled the substrate, indicating an increase in the bend transition temperature of D14 to above room temperature. The TRW coating alone was both protective and passed 90-degree bends after the long preoxidation treatments. The bend-test results for the other coating systems that were preoxidized were complicated by the high frequency of coating oxidation failures and attendant substrate contamination that occurred. Table 14 shows clearly that 50 hours at 2000 F or 10 hours at 2600 F approach the protective life of many of the coating systems. However, it is significant that most coated specimens that resisted oxidation failure passed the 90-degree bend test; the exception was the GT & E coating which embrittled the substrate even though the coating did not appear to have failed.

The effect of prestrain on the oxidation resistance of the coating systems was investigated by bending coated D14 specimens 2, 5, and 10 degrees with the 4T bend fixture and oxidation testing them at 2000 and 2600 F. The 2-degree bend was within the elastic range, but the specimens deformed plastically during the 5- and 10-degree bends. The coatings did not crack on specimen deflected 2 or 5 degrees, however all the coatings cracked and some spalled along the edges of the specimens during the 10-degree bends. Coating failures in the subsequent oxidation tests did not occur preferentially in the deformed region of specimens bent only 2 or 5 degrees, but the 10-degree bend did cause premature localized failure of most of the coatings.

Design Data Study of Coated FS85 Alloy. Based on the performance of the seven coating systems in the screening tests, the Pfaudler, TRW, and Vought coatings were selected for advanced evaluation on recrystallized 30-mil FS85 alloy, a medium-strength columbium alloy. The Vought coating was dropped from further consideration when it was observed that it provided less than 1-hour protection to FS85 at 2600 F (furnace oxidation test). Failure was accompanied by a molten oxide slag which destroyed the specimen. This was in marked contrast to the 6 to 13 hours' protection afforded by the coating on D14 at 2600 F (Table 14), suggesting that the difference may be due to substrate effects.

FS85 alloy sheet coated by TRW and Pfaudler was subjected to the following tests:

- (1) Oxidation
- (2) Combined thermal-shock and erosion test
- (3) Prestrain followed by oxidation
- (4) Tensile
- (5) Stress rupture.

The oxidation data for the two coatings in cyclic furnace tests are given in Table 15. Both coatings were protective for greater than 50 hours at 1600, 1800, 2000, and 2300 F, but the Pfaudler coating had only 4 hours' average life at 2500 and 2600 F whereas the TRW coating exhibited 130 and 50 hours' average life at the respective temperatures. The performance of the TRW coating was reproducible at all temperatures, but the Pfaudler coating had inconsistent life at 1800 F.

TABLE 15. PROTECTIVE LIVES OF PFAUDLER AND TRW COATINGS ON FS85 ALLOY IN CYCLIC OXIDATION TESTS^(a)

Oxidation Temperature, F	Lives of Replicate Specimens, hr ^(a)	
	Pfaudler	TRW
1600	>150, >150, >150	>150, >150, >150, >150
1800	21, 125, >150, >150	>150, >150, >150, >150
2000	>150, >150, >150, >150	>150, >150, >150, >150
2300	48, 48, 48, 56	>150, >150, >150, >150
2500	3, 3, 3, 5	117, 117, >150, >150
2600	1, 5, 5, 6	45, 51, 51, 51

(a) Specimens cycled to room temperature once each hour for 8 hours followed by 16 hours of static exposure in each 24-hour period. Tests stopped after 150 hours if specimens were unfailed.

Both coatings performed similarly in a test combining thermal shock and erosion. Curved sheet specimens were heated with an oxyacetylene torch to 2600 F in 20 seconds and cooled immediately to 250 F with an air jet at an average rate of 100 F/second. The Pfaudler and TRW coatings were protective during 500 of these thermal cycles. However, gross coating failure occurred in the maximum-temperature zone of specimens cycled 100, 250, and 500 times when the specimens subsequently were oxidized for 2 hours at 1600 F in a furnace. A lone exception was one TRW-coated specimen which resisted gross coating failure at 1600 F after 100 thermal cycles to 2600 F. Although both coating systems appeared resistant to thermal-shock failures, deficiencies in the thermal stability of coating protectiveness were defined.

Coated FS85 sheet was bent 2 degrees (elastic strain) and 5 degrees (plastic deformation) and oxidation tested at 2000 and 2600 F. Neither level of strain caused premature oxidation failure of either coating.

The deformation tolerance of the two coatings also was investigated by straining coated FS85 tensile specimens varying amounts at temperatures up to 2600 F, removing the load, and oxidation testing the strained specimens for 2 hours at 1600 or 2600 F. The test results are presented in Table 16. With only one exception in the entire series of tests, both coating systems withstood substantial plastic prestrains (greater than the proportional limit) without loss of subsequent 2-hour oxidation protection at 1600 or 2600 F.

TABLE 16. TOLERANCE OF PFAUDLER AND TRW COATINGS ON FS85 ALLOY TO DEFORMATION AT VARIOUS TEMPERATURES WITHOUT LOSS OF 2-HOUR OXIDATION PROTECTION AT 1600 AND 2600 F⁽²¹⁾

Prestrain Temperature, F	Proportional Limit, per cent strain	Limit of Tensile Prestrain Without Loss of 2-Hour Protection, per cent strain			
		TRW		Pfaudler	
		1600 F	2600 F	1600 F	2600 F
RT	2.2	6.4	4.5	3.3	3.0
400	1.8	4.1	5.5	3.1	2.7
800	1.6	>8.5	4.6	2.7	1.3
1200	1.4	>4.1	>4.1	2.1	2.3
1600	1.1	>2.0	>2.0	2.0	1.4
2000	1.1	7.0	>4.0	4.2	5.7
2300	1.1	25.8	18.0	<5.7	12.1
2600	1.1	>34.5	>37.3	<23.8	>38.5

Results of tensile tests of uncoated and coated FS85 sheet at temperatures up to 2600 F are presented in Figures 13, 14, and 15. The alloy was recrystallized prior to coating or testing in the uncoated condition. Coated specimens were tested in air; uncoated specimens were tested in vacuum at elevated temperatures. Both substrate-coating systems exhibited similar tensile properties. The yield and tensile strengths of coated specimens were less than those of uncoated specimens; however, only in the temperature range from 800 to 1600 F was this differential more than 5 to 10 per cent. The coatings eliminated the strain-aging peak of the substrate at 1200 F (Figure 13 and 14), but appeared to effect a phenomenon similar to strain aging at somewhat higher temperatures (1600 to 1800 F). (This anomaly has been reported to occur in Cb-1Zr alloy.) Ductility of coated specimens was somewhat lower than uncoated specimens;

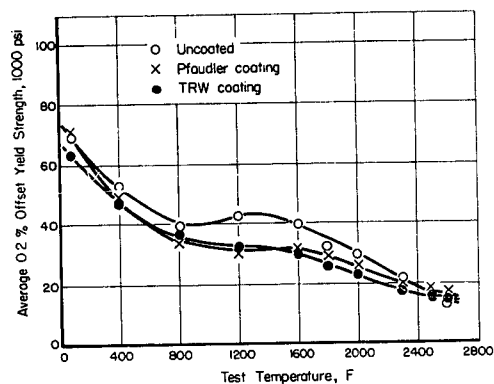


FIGURE 13. YIELD STRENGTH OF UNCOATED AND COATED 30-MIL FS85-ALLOY SHEET⁽²¹⁾

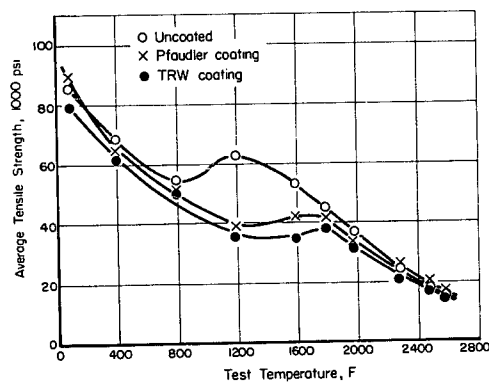


FIGURE 14. ULTIMATE TENSILE STRENGTH OF UNCOATED AND COATED 30-MIL FS85-ALLOY SHEET⁽²¹⁾

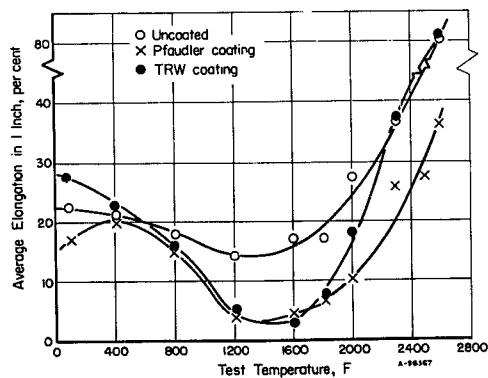


FIGURE 15. TENSILE ELONGATION OF UNCOATED AND COATED 30-MIL FS85-ALLOY SHEET⁽²¹⁾

this was most serious at temperatures of from 800 to 1800 F. Other tensile tests at 1200 F of specimens which had the Pfadler and TRW coatings stripped off resulted in restoration of the ductility obtained with the bare substrate (15 per cent). Hence the brittle coatings and/or diffusion zones, rather than the coating heat treatments caused the sharp drop in ductility at around 1200 F.

Tensile tests were repeated at 1200 F using another heat of FS85 that was lower in interstitial content (oxygen = 60 versus 150 ppm in original heat; carbon = 40 versus 250 ppm), because it was believed that the higher interstitial level of the first heat was responsible for the embrittlement of coated sheet at around 1200 F. The embrittlement persisted in spite of the reduction of the interstitial content in the second heat of FS85.

Stress-rupture data for coated specimens tested in air at temperatures of from 1600 to 2600 F are presented in Figures 16 and 17. The calculated stress to rupture in 10 or 100 hours, based on these data, is given in Table 17. Specimens coated by TRW had higher stress-rupture strength than those coated by Pfadler at 1600, 1800, 2500, and 2600 F, but the converse was true at 2000 and 2300 F (for times less than 75 hours at 2300 F). The stress-rupture strengths of coated specimens and bare FS85 sheet appear similar at 2000 and 2600 F although data for the base alloy are meager. Considerable elongation occurred during the tests without causing oxidation failures of either system. For instance, some specimens elongated 100 per cent at 2300 F without evidence of substrate oxidation. A significant side light is that coating oxidation life was considerably longer in the noncyclic exposures of the stress-rupture tests than it was in the cyclic oxidation tests described earlier. Both coatings exhibited lives of up to 100 hours at 2600 F in the stress-rupture tests.

TABLE 17. STRESS TO RUPTURE IN 10 AND 100 HOURS FOR PFAUDLER- AND TRW-COATED FS85 ALLOY TESTED IN AIR⁽²¹⁾

Test Temperature, F	Stress to Rupture, psi			
	Coated by Pfadler		Coated by TRW	
	10 Hours	100 Hours	10 Hours	100 Hours
1600	26100	24200	30500	29300
1800	26700	25900	28400	23300
2000	24500	18300	22300	17600
2300	16000	9500	13800	9800
2500	8900	3400	11600	6800
2600	8600	3100	9300	6250

Screening Evaluation of Coated D36 and B66 Foil⁽²³⁾

Solar has conducted an extensive screening evaluation of coated 6-mil foils of D36 (Cb-10Ti-5Zr) and B66 (Cb-5Mo-5V-1Zr) alloys. Coated TZM foil also is included in the program; these results are presented in the section on molybdenum. The immediate purpose was to ascertain the state of the art of coated foils. The long-range objective of this and other related programs is to be able to incorporate coated foils in honeycomb sandwich or monocoque construction for hot radiating surfaces of re-entry vehicles. The low-strength D36 alloy was chosen because it is readily available and can be rolled easily to foil. B66 was selected because it is fabricable, weldable, and has fairly high strength at elevated temperatures.

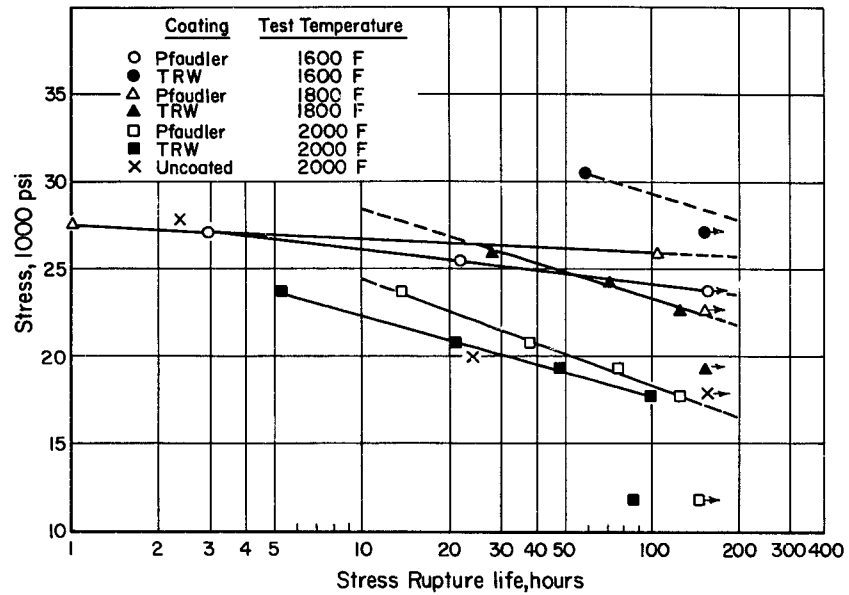


FIGURE 16. STRESS RUPTURE LIFE OF FS85 ALLOY COATED WITH PFAUDLER AND TRW COATINGS AND TESTED IN AIR AT 1600 TO 2000 F⁽²¹⁾

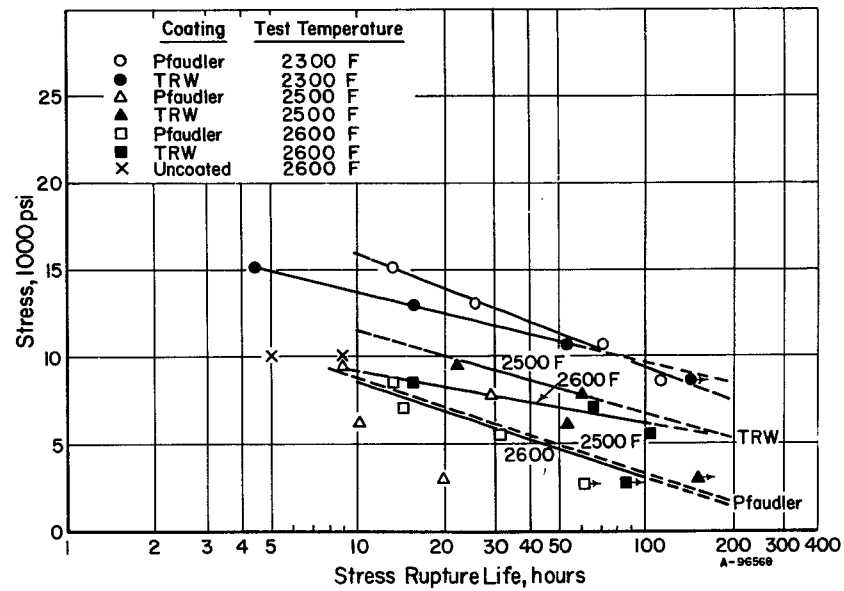


FIGURE 17. STRESS RUPTURE LIFE OF FS85 ALLOY COATED WITH PFAUDLER AND TRW COATINGS AND TESTED IN AIR AT 2300 TO 2600 F⁽²¹⁾

The coatings that were applied to the foils by outside organizations are described in Table 18. The coatings applied by GT & E were aluminum and tin base, and the balance of the coatings were modified silicides. The coating organizations were asked to apply coatings which would provide the best compromise between good oxidation resistance and mechanical properties. Only the D36 specimens coated by Vought were warped; the B66 specimens coated by Vought were not. Other coated specimens underwent little or no distortion. The coated specimens were evaluated by the following methods:

- (1) Weight and thickness of coating applied
- (2) Decrease in substrate thickness by diffusion interaction with coating during the coating process and oxidation tests
- (3) Cyclic oxidation of as-coated specimens at 2000 and 2500 F
- (4) Cyclic oxidation at 2000 and 2500 F of specimens previously bent over a 4T radius to a little below the outer fiber yield point
- (5) Plasma-torch oxidation tests at 2000 and 2500 F
- (6) Tensile tests of as-coated specimens
- (7) Bend tests of specimens in the as-coated condition and after static oxidation exposure at 2000 or 2500 F for about 85 per cent of the oxidation life in the cyclic tests [(3) above].

The weight of coating applied becomes increasingly important as sheet thickness is reduced to foil gages when considering strength-to-weight ratios. The coating weight ranged from 7 (GT & E coating on B66) to 52 per cent (GT & E coating on D36) of the weight of the substrate (Table 19). Another important consideration for foils is the reduction in substrate thickness by diffusion during coating and oxidation exposure, for this reduces load-carrying capacity. The data on residual substrate thickness are to be accepted with reservation, because they are single-value measurements and the diffusion fronts between the coating and/or diffusion zones and the substrate occasionally are jagged and therefore difficult to measure. In other instances the measurement of substrate thickness is an incomplete description of the structural effect of the coating on the substrate. Intergranular diffusion and formation of an intergranular phase also may adversely affect strength. The TRW coating effected substantial substrate consumption during coating (1.6 mils per side) but not during subsequent oxidation exposure at 2000 or 2500 F (Table 19). An intergranular phase formed throughout the D36 foil coated by TRW after being oxidized for 42 hours at 2500 F, but it did not occur in coated B66 that was oxidized for only 5 hours. The thick Sn-Al-Ta coating of GT & E reacted so extensively with the D36 substrate that the foil was consumed completely in 11 hours at 2500 F. In general, the other coatings consumed about 1 to 1.5 mils per side of the foil as a result of the coating process plus 5 to 10 hours' oxidation exposure at 2500 F.

The results of cyclic oxidation tests of as-coated specimens and specimens prestrained in bending are presented in Figures 18 and 19. Coating failures of unstrained specimens started predominantly at edges. Coating failures of prestrained specimens started in the bend area on about two-thirds of the specimens; the remaining failures were random. The TRW coating demonstrated superior oxidation resistance, protecting

TABLE 18. COATING SYSTEMS EVALUATED BY SOLAR ON 6-MIL D36- AND B66-ALLOY FOIL⁽²³⁾

Organization That Applied Coating	Average Coating Thickness, mils	Coating Process
<u>Coatings for D36 Alloy</u>		
Vought	2.0	Vought IV applied by 2-cycle pack-cementation process: (Cycle 1) siliconized 6 hr at 1950 F. (Cycle 2) Cr and B codeposited in 4 hours at 1950 F
General Telephone and Electronics (GT&E)	5.1	Painted with 95 (Sn-25Al)-5Ta metal powder in lacquer carrier and vacuum sintered 1/2 hour at 1900 F; coated and sintered twice
Chromizing	1.8	Durak KP; modified silicide coating applied by pack cementation in 12 hours at 1850 F
Thompson Ramo Wooldridge (TRW)	3.8	Two-cycle (Cr, Ti)-Si coating applied by vacuum pack cementation: (Cycle 1) Packed in Cr-Ti alloy powder and KF and heated for 4 hr at 2300 F, (Cycle 2) Siliconized in Si powder + KF for 4 hours at 2000 F
General Technology Corporation (GTC)	3.3 (Lot A) 1.6 (Lot B)	Three-cycle vacuum pack cementation: (Cycle 1) 20(Cr-Ti)-80 Al ₂ O ₃ pack for 10 hours at 2200 F, (Cycle 2) Si-Cb-Cr-B-W pack for 3 hours at 2000 F, (Cycle 3); repeat (2)
<u>Coatings for B66 Alloy</u>		
Vought	1.5	Vought IV applied by 2-cycle pack cementation: (Cycle 1) Si pack, 3-1/2 hr at 2000 F, (Cycle 2) Cr-B pack for 3-1/2 hr at 2000 F, specimens preoxidized 10 minutes at 2000 F
GT&E	2.3	(1) Vacuum pack titanized 16 hr at 2000 F, (2) hot dipped in aluminum alloy for 15 seconds at 1900 F, and (3) diffusion annealed 1 hr at 1900 F in argon
Chromizing	1.5	Durak KA
TRW	3.3	Same as for D-36
GTC	2.6	Three-cycle vacuum pack cementation: (Cycle 1) 20Ti, 80 Al ₂ O ₃ for 10 hours at 2100 F, (Cycle 2) 20Cr, 80 Al ₂ O ₃ pack for 10 hr at 2200 F, (Cycle 3) Si-Cb-Cr-B-W pack for 6 hr at 2000 F
Pfautler	1.8	Two-cycle pack cementation: (Cycle 1) chromized 7 hr at 2050 F, (Cycle 2) modifier + silicon for 5 hr at 2050 F

TABLE 19. THICKNESS OF COATINGS AND D36 AND B66 FOIL IN AS-COATED AND OXIDIZED CONDITIONS⁽²³⁾

Coating	Coating Thickness as Coated, mils	Coating Weight, per cent of foil weight	Residual Substrate Thickness				
			As Coated, mils	After 2000 F Oxidation		After 2500 F Oxidation	
				Hours	Thickness, mils	Hours	Thickness, mils
D36 Foil (5.75 ± 0.4 Mils, Prior to Coating)							
Chromizing	1.8	14	4.7	72	4.0	6	3.7
Vought	2.0	27	4.5	75	4.2	14	3.6
GT & E	5.1	52	5.0	75	1.4	11	0
TRW	3.8	35	2.4	75	1.8	42	2.7
GTC	1.6	25	4.2	--	--	--	--
B66 Foil (6.6 ± 0.4 Mils, Prior to Coating)							
Chomizing	1.5	12	5.3	57	5.0	6	4.3
Vought	1.5	14	5.0	33	4.5	6	4.5
GT & E	2.3	26	5.7	74	4.3	2	3.5
TRW	3.3	44	3.3	43	4.1	5	3.1
GTC	2.6	7	3.6	--	--	--	--
Pfaucler	1.8	16	5.2	75	5.3	6	4.1

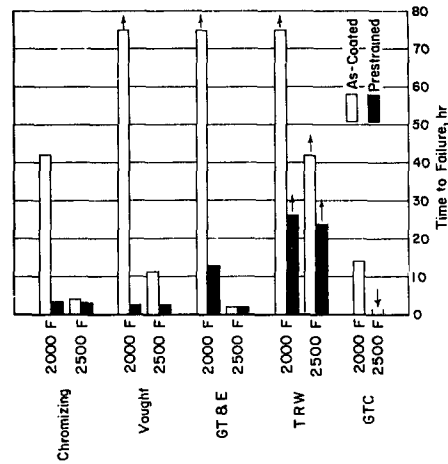


FIGURE 18. AVERAGE CYCLIC OXIDATION LIVES OF AS-COATED AND PRESTRAINED COATED D36 FOIL AT 2000 AND 2500 F⁽²³⁾

Furnace oxidation tests: specimens cycled to room temperature about once each hour; average of three specimens is reported.

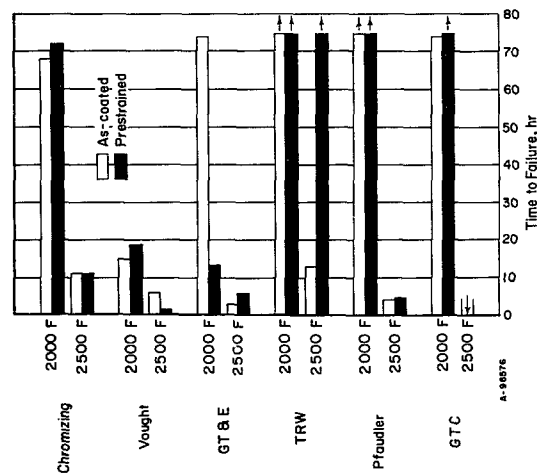


FIGURE 19. AVERAGE CYCLIC OXIDATION LIVES OF AS-COATED AND PRESTRAINED COATED B66 FOIL AT 2000 AND 2500 F⁽²³⁾

Furnace oxidation tests: specimens cycled to room temperature once each hour; average of three specimens is reported.

D36 and B66 for greater than 75 and 13 hours at 2000 and 2500 F, respectively, in both test conditions. Several coatings provided 75 hours' protection at 2000 F, but they were protective for only a few hours at 2500 F. The prestraining treatment effected greater reduction of oxidation life at 2000 F than it did at 2500 F, perhaps due to self-healing at the higher temperature.

The results of the plasma-torch oxidation tests at 2000 and 2500 F are given in Table 20. All the coatings except the one applied by Chromizing on D36 survived the 1-hour exposure at 2000 F. The 2-hour test at 2500 F approached the oxidation life of several of the coatings (Figures 18 and 19) and they (understandably) failed.

TABLE 20. RESULTS OF PLASMA-TORCH OXIDATION TESTS^{(a)(23)}

Coating	2000 F	2500 F
<u>D36 Foil</u>		
Chromizing	Failed by pest	Failed by pest in low-temperature zone
Vought	Passed	Passed
GT & E	Passed	Failed (burned through)
TRW	Passed	Passed
GTC	Passed	Failed (burned through)
<u>B66 Foil</u>		
Chromizing	Passed	Passed (some pits)
Vought	Passed	Failed (two of three specimens burned through)
GT & E	Passed	Failed (burned through)
TRW	Passed	Passed
GTC	Passed	Failed (burned through)
Pfandler	Passed	Passed

(a) Specimens positioned at 35 degrees to arc effluent of simulated air having velocity of 200 feet per second. Tests consisted of 4 to 15-minute cycles at 2000 F or 8 to 15-minute cycles at 2500 F.

The results of the tensile and bend tests are given in Figure 20 and Table 21. The yield and tensile strengths were calculated using the original thickness of the foil, so the reported values reflect effects due to the coating and to the reduction in substrate thickness effected by the coating operation. Some of the substrate-coating systems exhibited 90-degree bend angles in the 4T bend test and yet had very low ductility in the tension test. An example of this is the D36 foil coated by TRW which passed the 90-degree bend test but had nil ductility in the tensile test. A photomicrograph showed a crack extending through one-third of the substrate thickness of one of the bent specimens, but the specimen did not fracture completely. It appears that part of the discrepancy between ductilities measured by the tensile and bend tests is attributable to the method of defining failure in the bend specimens. The procedure recommended by the Materials Advisory Board for bend tests⁽²²⁾ specifies that initiation of a surface crack (not complete fracture) is the failure criterion. Undoubtedly it is difficult to distinguish a coating crack from a shallow substrate crack. The two GT & E coatings provided the best combination of strength and tensile elongation, but their extreme diffusion instability prognosticates sharply reduced strength after exposure at about 2500 F. The strengths of other substrate-coating systems generally were 80 per cent of those of the bare substrate, commensurate with the reduced substrate thickness and perhaps substrate strengthening. Tensile elongation was only 0 to 25 per cent of the bare foil.

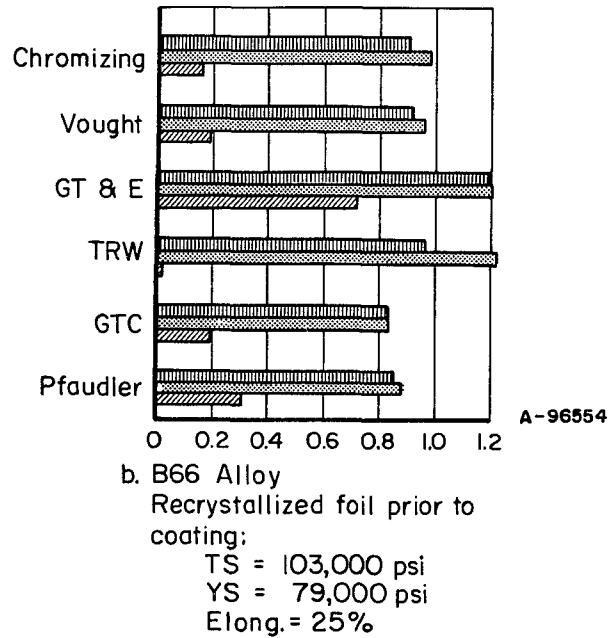
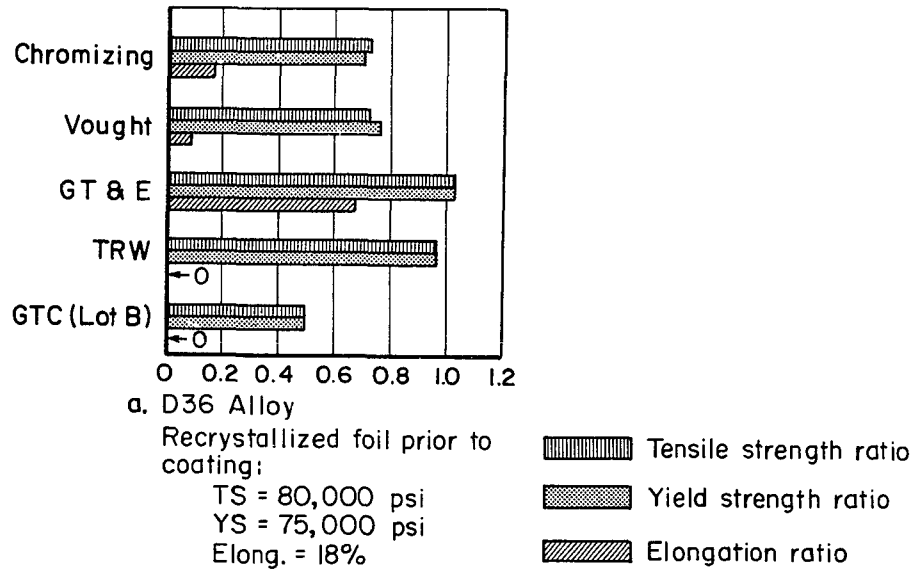


FIGURE 20. ROOM-TEMPERATURE TENSILE PROPERTIES OF AS-COATED D36 AND B66 FOIL⁽²³⁾

Strength values based on foil thickness prior to coating.

TABLE 21. ROOM-TEMPERATURE BEND TESTS OF COATED D36 AND B66 FOIL IN AS-COATED CONDITION AND AFTER OXIDATION EXPOSURE^{(a) (23)}

Coating	Bend Angle in As-Coated Condition, degrees	Bend Angle After Oxidation Exposure at Indicated Temperature			
		2000 F		2500 F	
		Oxidation Time, hr	Bend Angle, degrees	Oxidation Time, hr	Bend Angle, degrees
<u>D36 Foil</u>					
Bare substrate	90, 90	--	--	--	--
Chromizing	90, 90	42	90, 90, 90	7.0	90, 90
Vought	90, 90	64	90, 90, 90	7.0	90, 90
GT & E	90, 90	64	20, 28, 30	1.7	90, 90
TRW	90, 90	64	90, 90, 90	7.0	20, 20
GTC	36, 45	--	--	--	--
<u>B66 Foil</u>					
Bare substrate	90, 90	--	-- --	--	--
Chromizing	90, 90	22	90, 90, 90	4.5	90, 90, 90
Vought	44, 45	32	90, 90, 90	4.5	90, 90, 90
GT & E	90, 90	55	90, 90, 90	1.7	82, 85, 62
TRW	90, 90	29	90, 90, 90	1.7	90, 90, 90
GTC	42, 48	55	90, 90, 60	--	--
Pfautler	42, 53	30	90, 90, 90	1.7	90, 90, 90

(a) Test Procedure:

- (1) Specimens preoxidized in static furnace exposure (no cycling) for about 85 per cent of cyclic life of coating system.
- (2) Bend radius = 0.024 inch, nominal 4T bend radius. Tested according to procedure recommended by the Refractory Metals Sheet Rolling Panel of the MAB. Bend angle is the angle at which fracture occurred, or 90 degrees if specimen did not fracture.

Based on their performance in these screening tests, the following coatings currently are undergoing process optimization and advanced evaluation using 6-mil B66 foil:

- (1) Chromizing
- (2) GT & E
- (3) Pfudler
- (4) TRW.

COATINGS FOR MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

The following three molybdenum-base alloys are available commercially and they, along with unalloyed molybdenum, are the substrates that have been coated:

TZM - Mo-0.5Ti-0.08Zr
 TZC - Mo-1.25Ti-0.15Zr-0.15C
 Mo-0.5Ti

There is no indication that oxidation performance of the various coatings is affected by these low alloy additions. Mechanical tests (and oxidation tests) of coated molybdenum alloys are conducted at temperatures up to 3000 F because it is in the 2700 to 3000 F temperature range where the attractive strength-to-density ratio of molybdenum is particularly attractive. Most of the recent work on testing coatings for molybdenum alloys has been done with TZM, because it is readily available in sheet form and because of its favorable rating in considerations such as strength, fabricability, transition temperature, and recrystallization temperature.

Test Data for Individual Coatings

W-3 Coating

The W-3 coating is Chromalloy's latest and best modified silicide coating⁽¹⁰⁾, and is applied by a proprietary pack-cementation process. Oxidation life of the W-3 coating on 35-mil Mo-0.5Ti sheet coupons in cyclic furnace tests has been reported by Chromalloy⁽¹⁰⁾ as follows:

Test Temperature, F	Coating Thickness, mils	Time to Coating Failure, hr		
		Minimum	Maximum	Average
2500	3.5	732	931	812
2700	3.4	26	395	268
3000	1.2	1.25	3.75	2.85

The 3.5-mil coating tested at 2500 and 2700 F were abnormally thick compared to the 2-mil W-3 coatings being applied for vehicle applications such as ASSET. The 3000 F test results may not be representative of the W-3 coating, because a reaction between the specimens and ceramic supports caused localized failures. McDonnell has reported that a 1.3-mil-thick W-3 coating protects TZM substrate from oxidation for a minimum of 2 hours at 3100 F at atmospheric pressure or 30 minutes at 3000 F under 0.07 mm air pressure⁽²⁴⁾. A comparison of the oxidation lives of W-3 and W-2 (an earlier commercial variety) coatings on Mo-0.5Ti substrate at atmospheric pressure is shown in Figure 21⁽¹⁰⁾. While there was little practical difference in the minimum coating life, about 60 per cent of the W-3-coated samples exhibited lives of from 6 to 8 times longer than the W-2 coating.

The W-3 coating has been oxidation tested at low air pressures by resistance heating of coated 25-mil molybdenum wires in a vacuum chamber⁽²⁵⁾. The test results are shown in Figure 22. The reported temperatures are uncorrected optical values, so the true temperatures probably were somewhat higher. The W-3 coating resisted failure at 1 mm air pressure for 15, 30, and 100 minutes at optical temperatures of 3000, 2900, and 2800 F, respectively. For comparison, under atmospheric pressure the average life of similarly tested specimens was 3.8 hours at 3000 F.

Results of tensile tests of W-3-coated TZM sheet conducted in air at temperatures up to 3000 F⁽²⁶⁾ are given in Table 22. Some specimens were uncoated (tested in inert atmosphere); others were coated twice. Still others were coated, oxidation proof tested for 1/2 hour at 2000 F, and finally coated again. Tensile properties at room temperature were not degraded significantly by either coating sequence. Elongation

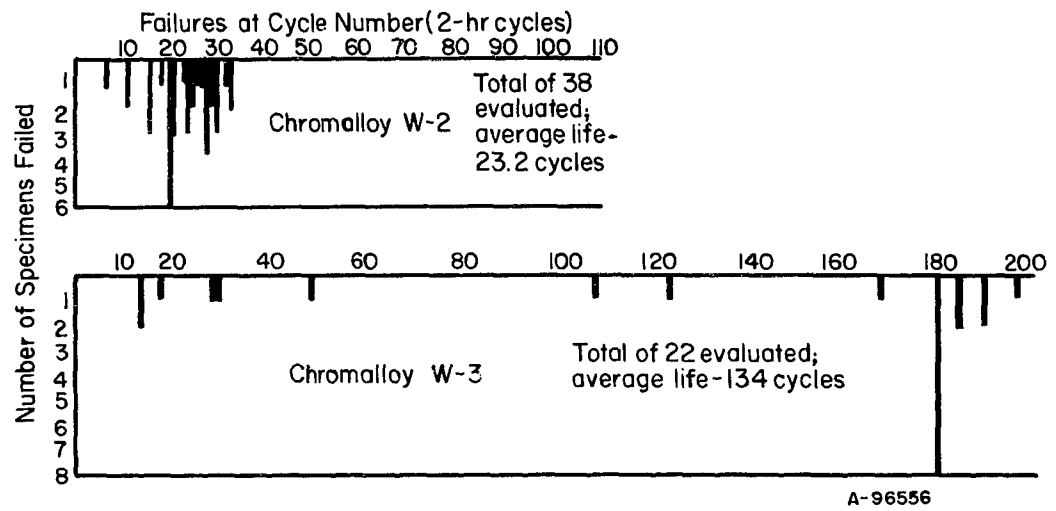


FIGURE 21. 2700 F CYCLIC OXIDATION LIVES OF CHROMALLOY'S W-2 AND W-3 COATINGS ON Mo-0.5Ti ALLOY IN SLOWLY MOVING AIR⁽¹⁰⁾

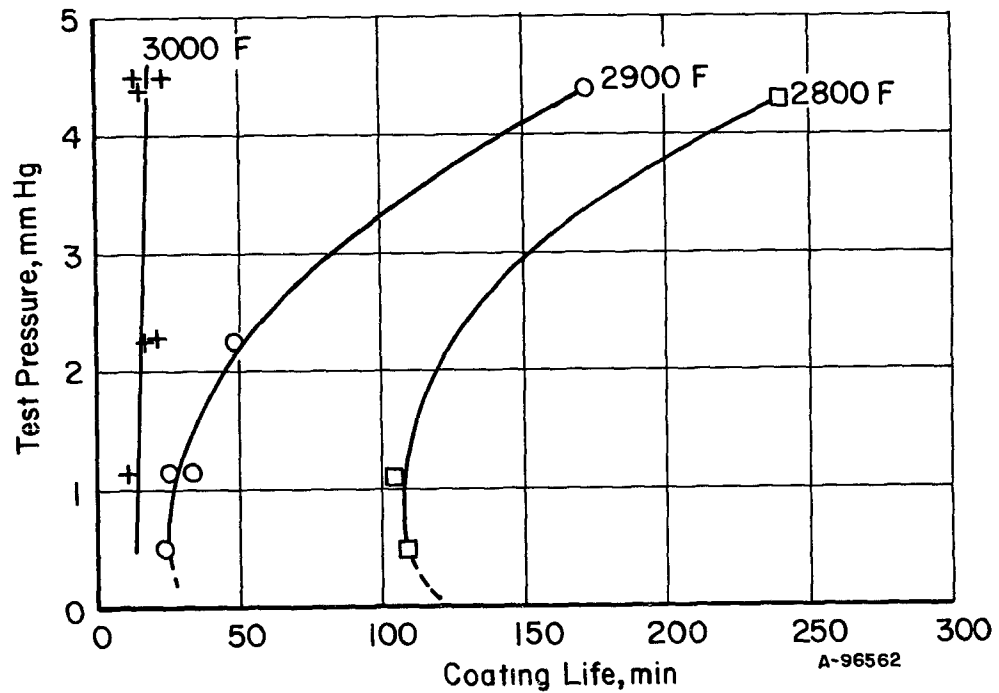


FIGURE 22. PROTECTIVE LIFE OF W-3 COATING ON MOLYBDENUM IN LOW-PRESSURE OXIDATION TESTS⁽²⁵⁾

Temperatures are uncorrected optical values.

decreased as test temperature was increased, perhaps due to strain-induced coating failures. The relatively high strengths obtained indicate that the wrought structure of TZM was retained during the coating process. At 2500 F, where some recrystallization during testing is probable, strength values were most erratic; at lower or higher temperatures strengths were more reproducible. The coating was not significantly detrimental to the tensile behavior of TZM in these tests. The very low ductility at 1800 F (1 per cent) is not understood, but it may be a response to an equicohesive temperature condition that is accentuated by the coating.

TABLE 22. TENSILE PROPERTIES OF 20-MIL TZM SHEET COATED WITH 2-MIL W-3 COATING AND TESTED IN AIR^(a) (26)

Condition of Specimen ^(b)	Test Temperature, F	Yield Strength, psi	Ultimate Strength, psi	Elongation in 2 Inches, per cent
Uncoated	RT	118,000	135,000	9
"	RT	122,000	135,000	8
"	RT	121,500	135,000	7(c)
"	RT	124,500	138,000	8(c)
C-O-C	RT	110,500	124,000	8(c)
C-O-C	RT	119,500	122,500	(c)
C-C	RT	119,000	127,000	7(c)
C-C	RT	117,000	127,000	7
C-O-C	400	94,000	105,000	4
C-O-C	400	93,000	107,000	6(c)
C-C	400	90,500	105,000	5
C-C	400	90,000	103,500	4
C-O-C	1800	76,000	82,000	1
C-O-C	1800	73,000	79,500	--
C-C	1800	74,000	85,500	1(c)
C-C	1800	72,500	78,500	1
C-O-C	2500	18,500	22,000	(d)
C-O-C	2500	35,000	39,000	(d)
C-C	2500	17,000	22,500	(d)
C-C	2500	23,000	27,500	(d)
C-O-C	3000	8,500	9,500	(d)
C-O-C	3000	9,000	11,500	(d)
C-C	3000	12,500	--	(d)

(a) Specimens soaked 30 minutes at test temperature before testing. Strengths based on area before coating.

(b) C-O-C = coated, then oxidation check tested 30 minutes at 2000 F, then coated again; C-C = coated twice without intermediate oxidation check.

(c) Specimen failed outside gage length.

(d) Oxidation in failure area was too extensive to measure elongation.

W-2 Coating

Chromalloy has been granted a patent covering its W-2 coating⁽²⁷⁾ which has been applied predominantly to molybdenum and its alloys. The coating is applied by the pack-cementation process using the following pack composition;

6 per cent chromium
11 per cent silicon

0.25 per cent NH_4I
83 per cent Al_2O_3 .

Parts to be coated are placed in the particulate mix in a metal retort. The retort becomes sealed with a fusible silicate as it is heated to 1400 F in a furnace. A typical coating temperature is 2000 F. X-ray diffraction analysis of the coating indicates that the major coating phase is MoSi_2 , and there are thin diffusion layers of Mo_5Si_3 and Mo_3Si between the MoSi_2 layer and the substrate⁽²⁸⁾. The chemical analysis of the coating⁽²⁷⁾, in atomic per cent is

Molybdenum = 30.5
Silicon = 69
Chromium = 0.5 ,

which approximates MoSi_2 .

The Douglas Aircraft Company⁽²⁹⁾ has conducted preliminary studies concerning the effect of a 0.001-inch-thick W-2 coating on the crack propagation and residual strength of cracked molybdenum sheet. Fatigue cracks were grown in 2 by 6-inch panels of 0.050-inch-thick sheet with a 0.40 by 0.010-inch slot cut into the center of the specimen. Typical fatigue-crack growth curves for coated and uncoated specimens of the same lot are illustrated in Figure 23. The uncoated specimens were cycled at a stress level of 40,000 psi, whereas the coated specimens were cycled at 25,000 psi. Figure 24 shows that variations in crack growth characteristics among the several sheets examined were considerably larger for the coated specimens. The scatter was attributable largely to variations in the crack nucleation period rather than to variations in the growth rates of the cracks. Figure 24 also shows that the lower limit of the scatter band for coated panels merges with the upper limit of the scatter band for uncoated panels in spite of the fact that the coated panels were cycled at 15,000-psi lower stress. This observation indicates that the application of an oxidation-resistant coating may make crack nucleation and propagation considerably easier and thereby tends to embrittle the material. In this connection, it was reported that coated panels tended to shatter when accidentally struck with light impact loads at room temperature.

Figure 25 illustrates the effect of degree of cracking on the residual strength of coated molybdenum panels tested in air at high temperatures. The Douglas interpretation that the strength decreases with increasing crack length is as would be expected due to reduction of the cross-sectional area supporting the load. The scatter, which is particularly great at 1600 F, makes interpretation difficult, and tends to impugn the effect of soak time (at 2000 F) cited in Figure 25.

PFR-6 Coating

Pfaudler's PFR-6 coating is applied in a one-cycle pack-cementation process in a pack containing particulate silicon and columbium. Thickness of the coating can be varied by altering coating time, temperature, or pack composition. Pfaudler has evaluated the high-temperature oxidation resistance of the coating on Mo-0.5Ti sheet in oxyacetylene-torch tests⁽³⁰⁾. Coated specimens 1.5 by 3 inch were heated to 3000 F with the flame and then quenched to room temperature with an air jet after every 0.5-hour exposure period. Coating weight gain was proportional to coating thickness (5 to 6 mg/cm^2 is equivalent to 1 mil of silicic coating), and Figure 26 shows that coating life increased with coating thickness.

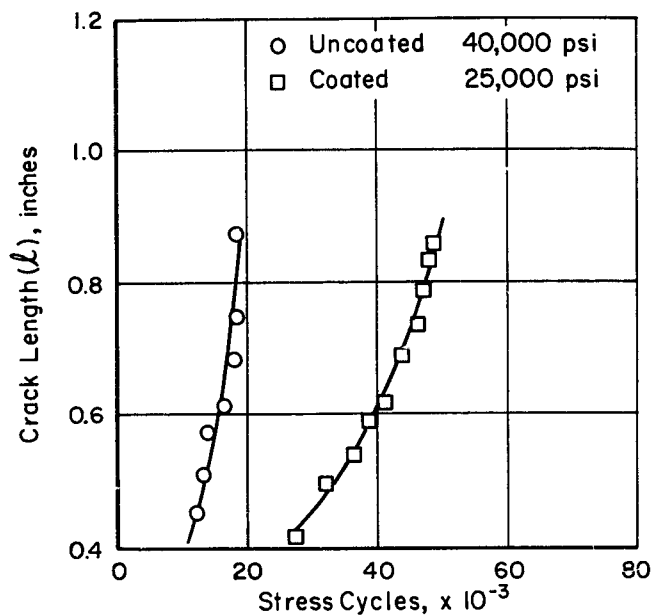


FIGURE 23. TYPICAL FATIGUE-CRACK GROWTH IN SPECIFIC PANELS OF COATED AND UNCOATED MOLYBDENUM AT 80 F⁽²⁹⁾

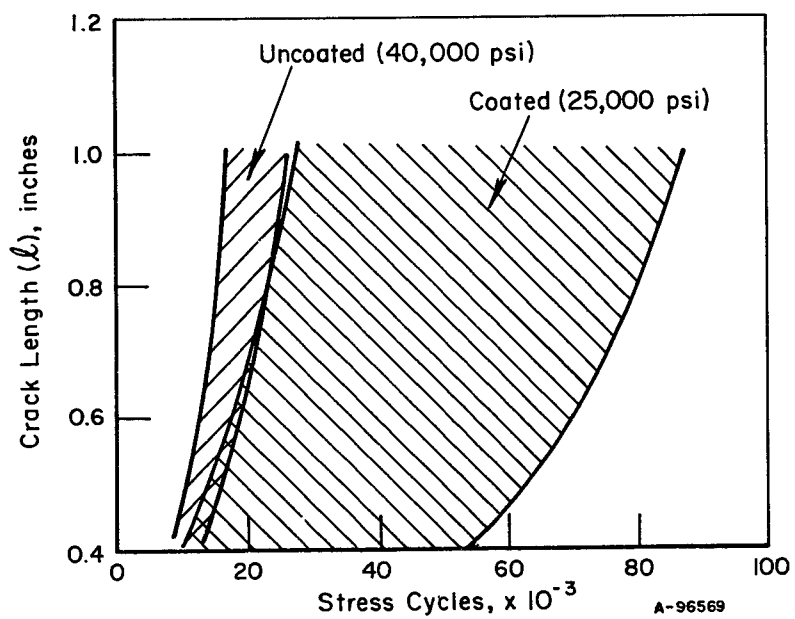


FIGURE 24. SCATTER IN THE CRACK-GROWTH CHARACTERISTICS OF SEVERAL COATED AND UNCOATED MOLYBDENUM SHEETS AT 80 F⁽²⁹⁾

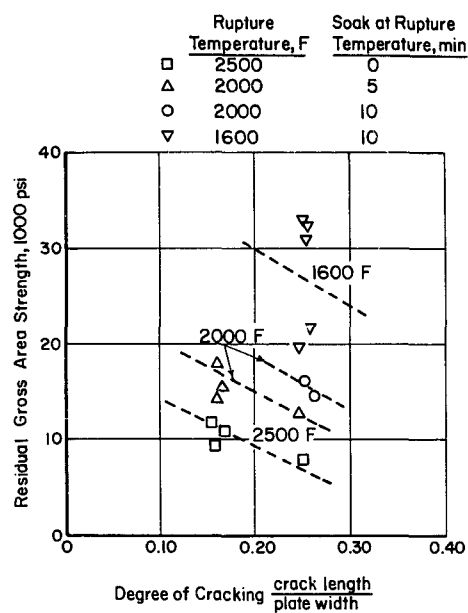


FIGURE 25. RESIDUAL STRENGTH OF COATED PANELS VERSUS DEGREE OF CRACKING⁽²⁹⁾

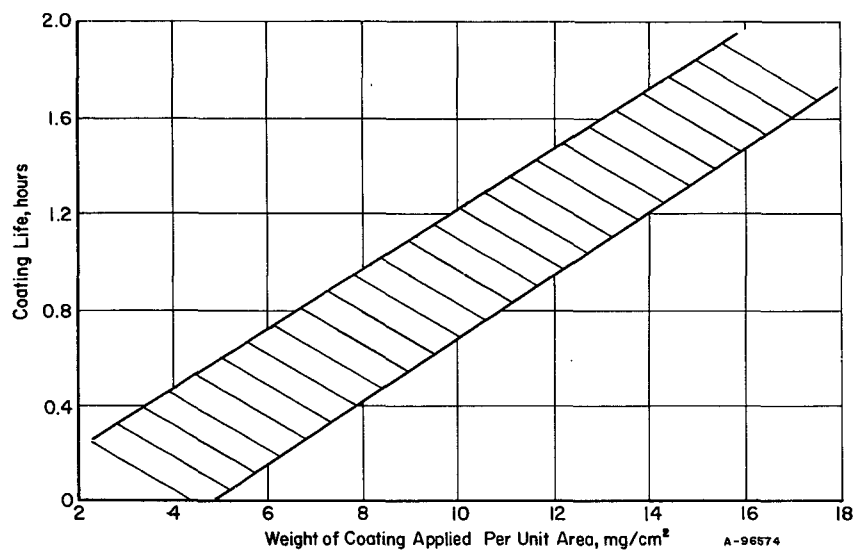


FIGURE 26. OXIDATION LIFE OF PFR-6 COATING ON 30-MIL Mo-0.5Ti SHEET IN 3000 F OXYACETYLENE-TORCH TEST⁽³⁰⁾

5 to 6 mg/cm² \approx 1 mil of disilicide coating.

The PFR-6 coating also was tested on Mo-0.5Ti and TZM sheet at low temperatures to check for the occurrence of pest failure⁽³⁰⁾. Pest was not observed when coated Mo-0.5Ti specimens were exposed consecutively for periods of 3 hours each at 50 F temperature increments from 1100 to 1650 F (total exposure = 36 hours). Coated TZM sheet also was exposed for 24-hour periods at temperatures ranging from 800 to 1300 F. Only the specimen exposed 24 hours at 1100 F had irregular oxidation performance. A large weight gain and increase in thickness accompanied formation of a white oxide on the coating. This phenomenon was not duplicated in even 100 hours on coated Mo-0.5Ti or other TZM specimens in another oxidation test at 1100 F. Other noncyclic furnace oxidation tests of the PFR-6 coating on Mo-0.5Ti sheet showed that it resisted pest failure for more than 50 hours at 1500 F, but pinhole coating failures occurred on 6 out of 16 specimens during the 50-hour exposure period⁽⁴⁾. The oxidation life of PFR-6 coating as determined in furnace oxidation tests at 2400, 2600, and 2800 F is given in Table 23. There is appreciable scatter in the coating-life data. The coating failed most frequently at edges, and edge failures generally occurred earlier than failures on flat surfaces.

TABLE 23. OXIDATION LIFE OF PFR-6 COATING ON Mo-0.5Ti SHEET IN CYCLIC FURNACE OXIDATION TESTS (a) (4)

Temperature, F	Sheet Thickness, mils	Coating Life, hr	Failure Location
2400	50	> 50, > 50, > 50,	No failure
2400	50	28	Edge
2400	10	40	Flat surface
2400	10	7, 10, 10	Edge
2600	50	48	Flat surface
2600	50	2 ^(b) , 2 ^(b) , 14, 15, 22	Edge
2600	10	14, 22 ^(b) , 32	Flat surface
2600	10	12, 12 ^(b) , 14	Edge
2800	50	12,	Flat surface
2800	50	1 ^(b) , 2 ^(b) , 2, 6, 12	Edge
2800	10	2 ^(b)	Flat surface
2800	10	1, 1, 2, 2, 2 ^(b)	Edge

(a) Specimens cycled to room temperature at 1-hour intervals.

(b) Preoxidized 50 hours at 1500 F without failure.

General Dynamics ascertained the stress-rupture strength of Mo-0.5Ti sheet coated with PFR-6⁽²⁴⁾. Test specimens were resistance heated and optical pyrometer temperature was corrected assuming emittance to be 0.9. The 30-minute stress-rupture strength at 2800 F was about 7,400 psi. The coating demonstrated capability for protecting the substrate from oxidation for greater than 30 minutes at 2800 F while undergoing 1.5 to 4 per cent creep. Stress-rupture data for 20- and 50-mil Mo-0.5Ti sheet coated with PFR-6 and tested in air at 2400, 2500, and 2600 F as shown in Figure 27.

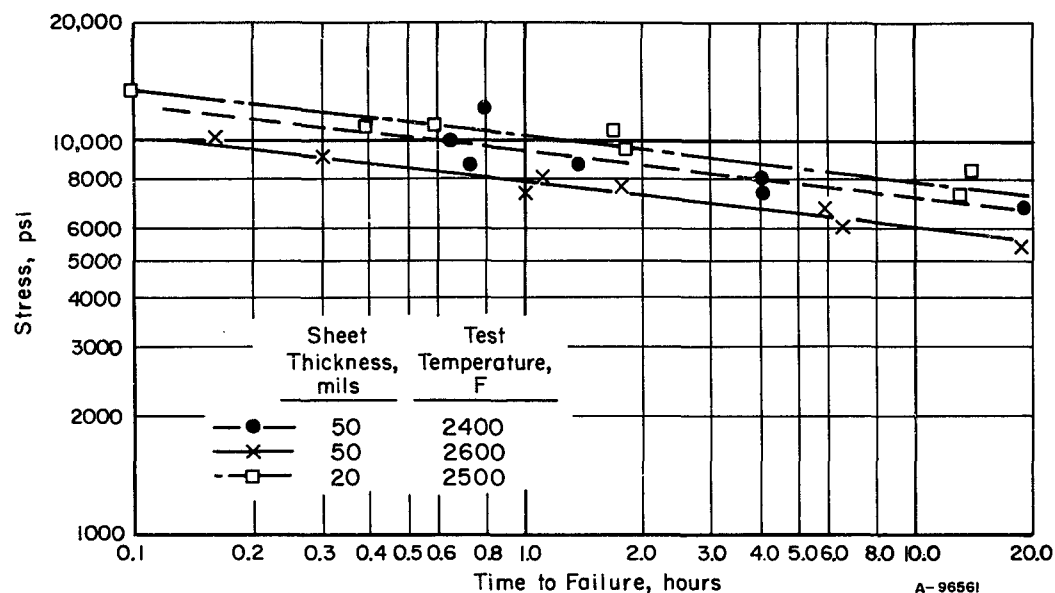


FIGURE 27. STRESS-RUPTURE STRENGTHS OF 50-MIL Mo-0.5Ti COATED WITH PFR-6 TESTED IN AIR⁽⁴⁾

Durak-B Coating

Durak-B is a modified silicide pack-cementation coating of the Chromizing Corporation. Table 24 gives some room-temperature tensile properties of TZM alloy coated with Durak-B. Elongation dropped from 20 to 2 per cent as a result of applying the coating⁽¹⁶⁾. The yield and tensile strength decreased only slightly in the as-coated condition, but they dropped about 35 per cent after oxidation exposure at 2750 F, as a consequence of recrystallization.

TABLE 24. ROOM-TEMPERATURE TENSILE PROPERTIES OF TZM MOLYBDENUM ALLOY COATED WITH DURAK-B⁽¹⁶⁾

Condition of Test Specimen	Room-Temperature Strength, 1000 psi		Elongation in 2 Inches, per cent
	Ultimate	0.2% Yield	
Uncoated	117	104	20
As coated	105	100	2
Coated and oxidized 2 hr at 2750 F	74	66	5

Boeing Silicide Coating⁽⁵⁾

Boeing's straight silicide coating, sometimes called Disil, is applied by a fluidized-bed process. The oxidation protection afforded by the coating in oxyacetylene-torch tests was presented in Figure 4. Minimum coating life is 4 hours at 2700 F or 2.5 hours at 3000 F (uncorrected optical temperatures).

Vitro Nickel-Modified Silicide Coating⁽³¹⁾

Vitro has a coating for molybdenum that is applied by electrophoretic deposition. Particulate material having the composition $94\text{MoSi}_2\text{-}6\text{Ni}$ is applied to the substrate by this process, and then the coated parts are pressed isostatically under pressures of 10 to 30 tons/in.² to densify the coating. Further densification and bonding occur in a subsequent sintering treatment at about 2300 F. The coating has protected 1/4-20 TZC bolts from oxidation for up to 40 hours at 2500 F.

Other Coatings

The coatings for molybdenum for which little or no recent information is available from the producer, but which have been tested in the comparative evaluation programs presented in the next section, are as follows:

American Machine & Foundry, AMFKOTE-2 - pack cementation, modified silicide

Chance Vought, Vought IX (now obsolete) - pack cementation, modified silicide

Chromizing, Durak-MG - pack cementation, modified silicide

General Technologies Corp. - pack cementation, modified silicide

General Telephone & Electronics - Sn-Al slurry coating, modified with molybdenum

Pfautler, PFR-5 - pack cementation, modified silicide.

Comparative Evaluations of Coatings

Comparative Evaluation of Coatings on Mo-0.5Ti Sheet^(32, 33)

Langley Research Center (NASA) has conducted a comparative screening evaluation of 6 coating systems on 12-mil stress-relieved Mo-0.5Ti sheet as part of an overall program to define the utility of coated thin-gage refractory-metal sheet for hot surfaces of aerospace vehicles. Sheet specimens were tumbled in an abrasive mixture to round the edges in preparation for applying the coatings. The coatings that were tested are described in Table 25. The coatings were fairly thin, ranging from 1.2 to 2.3 mils, and the substrate thickness was decreased from 10 to 25 per cent by the various coating processes.

TABLE 25. COATING SYSTEMS EVALUATED ON 12-MIL MO-0.5Ti SHEET BY LANGLEY RESEARCH CENTER(32, 33)

Organization That Applied Coating	Coating Designation	Constituent Elements	Method of Application	Metallographic Coating Thickness, mils	Metallographic Substrate Thickness			Weight Change During Coating, per cent
					Before Coating, mils	After Coating, mils	Decrease, per cent	
American Machine & Foundry	AMFKOTE-2 (preoxi- dized(a))	Si, B, Cr, Cb, Al, C	Two-cycle pack cementation	1.7	12.2	9.2	24	2.2
American Machine & Foundry	AMFKOTE-2	Ditto	Ditto	1.7	12.2	9.9	18	2.2
Boeing	Disil	Si	Fluidized bed	1.5	10.8	8.1	25	-3.8(b)
Chance Vought	IX(c)	Si, Cr, B, C, Al, Ti, Cb	Two-cycle pack cementation	1.4	12.0	10.6	12	3.4
Chromalloy	W-2	Si, Cr	Two-cycle pack cementation	1.2	12.1	10.9	10	4.4
Pfandler	PFR-5	Si, Cr	Two-cycle pack cementation	2.3	11.8	9.1	23	13.7
Pfandler	PFR-6	Si, Cb	One-cycle pack cementation	1.9	11.6	9.7	16	7.9

(a) Preoxidized 1 hour at 2800 F to form glassy oxide.

(b) Weight loss apparently due to removal of substrate by Boeing during cleaning operation in preparation for coating.

(c) Vought IX coating now is obsolete.

The oxidation life of the coatings in cyclic and noncyclic furnace oxidation tests at 2300 F is shown in Figure 28. The data are reported in terms of oxidation time to 10 per cent weight loss (due to molybdenum oxide volatilization) as an expedient in establishing coating failure time. Cycling to room temperature at 1.0- and 0.1-hour intervals decreased coating life considerably compared to that obtained in noncyclic exposure. AMFKOTE-2 exhibited superior oxidation resistance, followed by the Pfaudler coatings.

Room-temperature tensile properties of as-coated specimens are compared to those of the bare substrate in Figure 29. Yield and tensile strengths were calculated using the thickness of the uncoated sheet. Considering that the substrate thickness was reduced by applying the coatings (Table 25) only the AMFKOTE and probably the Pfaudler coatings reduced the strength of the residual substrate. Substrate ductility was retained in Disil-, Vought-, and Pfaudler-coated specimens, but was degraded by the W-2 coating and even more seriously by AMFKOTE-2.

The reduction in substrate thickness by diffusion interaction with the coatings during oxidation exposure at 2500 F is given in Figure 30. As each point represents only one observation, full reliance on the data shown is hazardous. Generally, assuming that coatings were applied at temperatures appreciably less than 2500 F, the expected effects of both temperature and time were approximated, although there are discrepancies that are best rationalized by assuming that specific data points are not representative. From the data shown one might conclude that the Vought and perhaps the AMFKOTE coatings have somewhat superior diffusional stability.

Screening Evaluation of Coated TZM Foil⁽²³⁾

The program at Solar to evaluate coated foils, which was outlined in the section on columbium, also included 6-mil TZM foil. Test procedures were the same as those described earlier. Table 26 describes the coating systems that were investigated.

The TZM foil was in the stress-relieved condition prior to coating. None of the coating processes brought about significant recrystallization, with the exception of the Vitro coating. The sintering operation at 2300 F for this coating resulted in partial recrystallization in the TZM adjacent to the coating, apparently due to depression of the recrystallization temperature by inward diffusion of nickel from the coating.

Only the GT & E tin-aluminum coating effected a large increase in the weight (47 per cent). The weight of the silicide coatings ranged from 6 to 19 per cent of the weight of the foil as shown in Table 27. The reduction in the foil thickness by diffusion during application of the coatings and during subsequent oxidation exposures is also given in Table 27, and indicates superior diffusional stability for the Vitro, Chromalloy, and Chromizing coatings compared to the other silicide coatings. The GT & E coating effected relatively rapid diffusion consumption of the foil substrate, based on these data.

The results of cyclic furnace oxidation tests of as-coated and prestrained (specimens bent over 4T radius at room temperature to just below the outer fiber yield point) specimens are shown in Figure 31. All coatings except GT & E and AMF protected unstrained specimens for 50 hours at 2000 F. Protective life was reduced to only a few hours at 2500 F, with the exception of the 50 hours' life exhibited by the Vitro coating. Most coating failures of prestrained specimens occurred preferentially in the bend

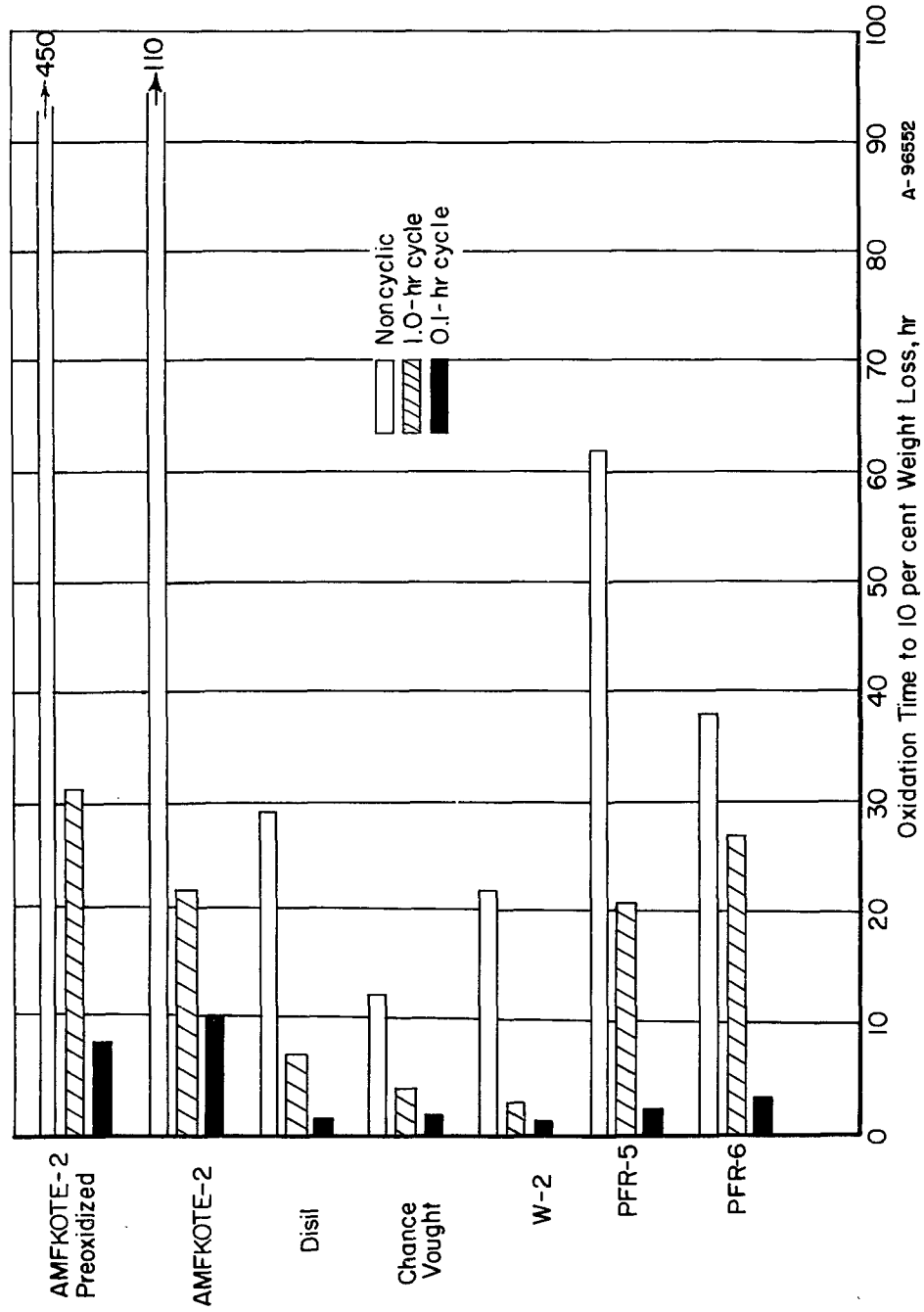


FIGURE 28. OXIDATION LIFE OF COATINGS ON 12-MIL Mo-0.5Ti SHEET IN CYCLIC AND NONCYCLIC FURNACE TESTS(33) AT 2500 F

Failure time arbitrarily selected as time at which 3/4 x 1-1/2 inch specimen lost 10 per cent weight.

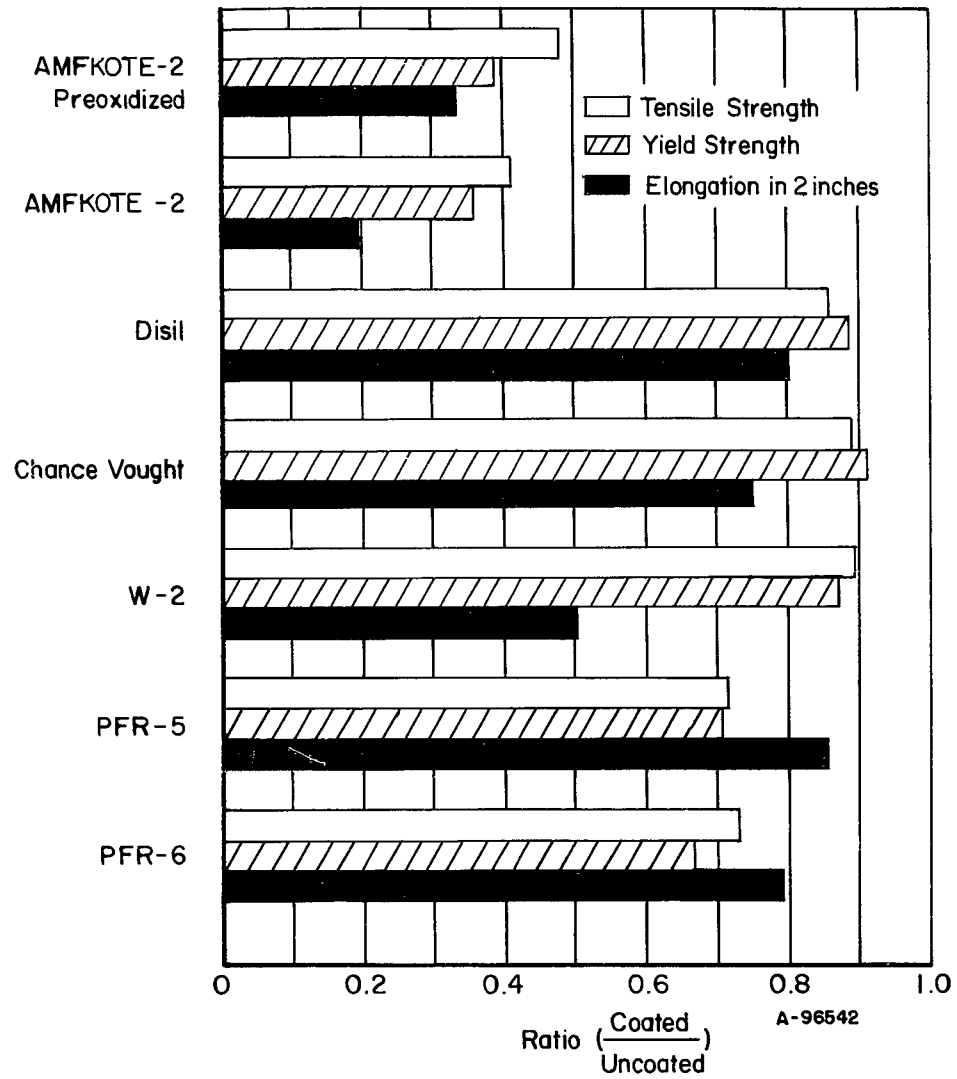


FIGURE 29. ROOM-TEMPERATURE TENSILE PROPERTIES OF AS-COATED Mo-0.5Ti SHEET⁽³³⁾

Strength values based on foil thickness prior to coating.

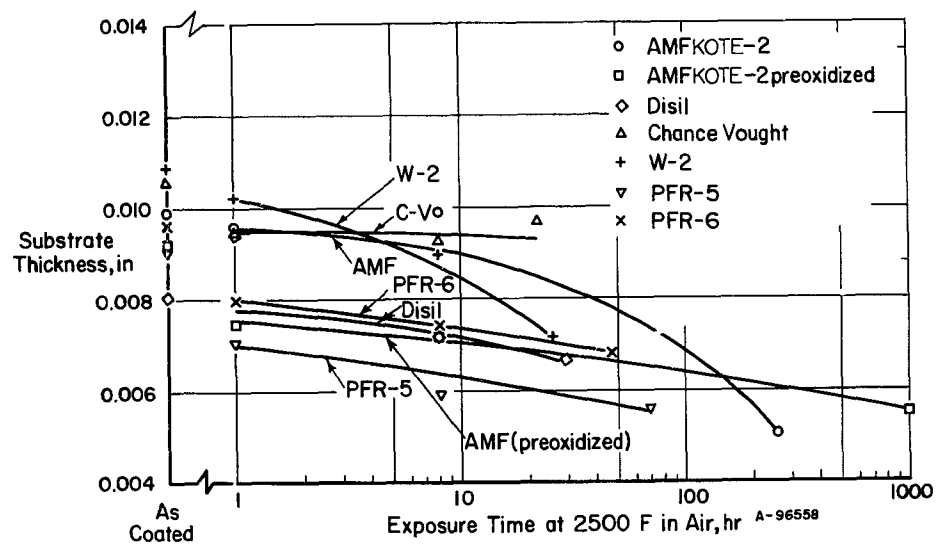


FIGURE 30. DIFFUSION DEPLETION OF COATED Mo-0.5Ti SUBSTRATE DURING 2500 F OXIDATION EXPOSURE⁽³³⁾

TABLE 26. COATING SYSTEMS EVALUATED BY SOLAR ON 6-MIL TZM FOIL⁽²³⁾

Organization That Applied Coating	Average Coating Thickness, mils	Coating Process
Chromizing	1.4	Durak B
Vought	2.1	Vought IV, applied by 2-cycle pack cementation: (Cycle 1) siliconized 5 hr at 1900 F; (Cycle 2) Cr-B applied in 5 hr at 1900 F
General Telephone & Electronics (GT&E)	3.2	Painted with Sn-25Al-5Mo-2Si metal powder in lacquer carrier and vacuum sintered 1/2 hr at 1900 F
General Technologies Corporation (GTC)	2.0	Pack-cementation process using pack containing Si, Cr, Cb, W, and Al ₂ O ₃ for 6 and 4 hr (2 cycles) at 2000 F
Pfautler	2.0	PFR-6 applied by pack cementation, pack contains Si, Cb, Al ₂ O ₃ , and halide carrier; 1 hr at 1850 F and 7 hr at 2050 F
Chromalloy	1.1	W-3 which is a modified silicide coating applied by pack cementation
AMF	1.4	AMFKOTE-2 which is a modified silicide coating applied at 1975 F
Vitro	3.1	⁹⁴ MoSi ₂ -6Ni composition applied by electrophoretic deposition; coating is isostatically pressed at 15,000 psi and then sintered in argon for 1 hr at 2300 F

TABLE 27. THICKNESS OF COATINGS AND TZM FOIL^(a) IN AS-COATED AND OXIDIZED CONDITIONS⁽²³⁾

Coating	Coating Thickness As Coated, mils	Coating Weight, per cent of foil weight	Residual Substrate Thickness				
			As Coated, mils	After 2000 F Oxidation		After 2500 F Oxidation	
				Hours	Thickness, mils	Hours	Thickness, mils
Chromizing	1.4	--	4.7	75	4.6	15	3.9
Vought	2.1	19	3.8	75	3.2	31	1.9
GT&E	3.2	47	5.5	18	4.6	6	3.0
GTC	2.0	15	4.3	75	2.6	6	3.4
Pfautler	2.0	15	4.7	59	4.1	11	3.2
Chromalloy	1.1	6	5.1	72	4.4	7	4.6
AMF	1.4	11	4.6	3	4.4	1	4.5
Vitro	3.1	--	4.5	75	4.5	56	3.1

(a) TZM foil was 6 ± 0.6 mils thick prior to coating.

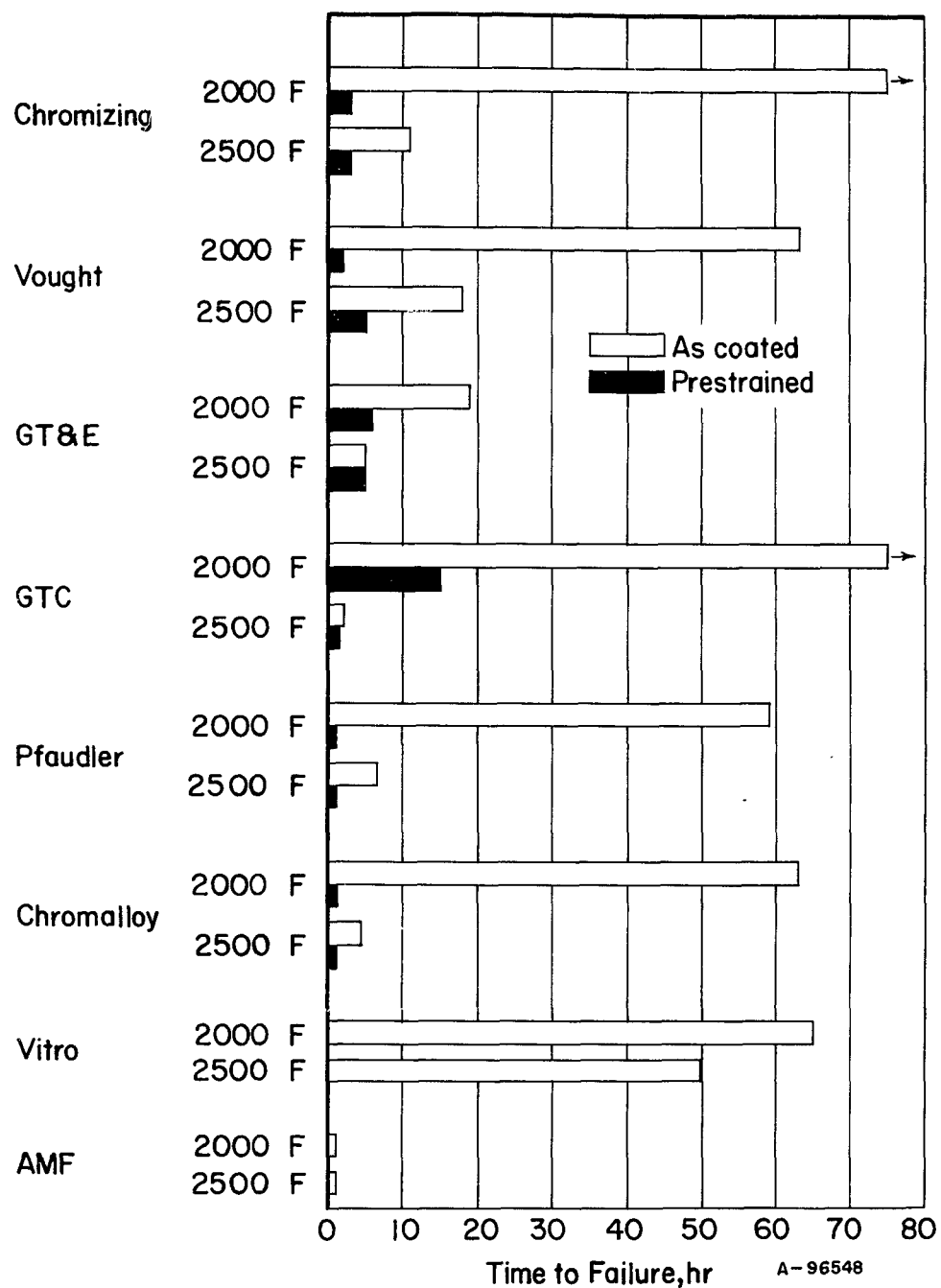


FIGURE 31. AVERAGE CYCLIC OXIDATION LIVES OF AS-COATED AND PRESTRAINED COATED TZM FOIL AT 2000 AND 2500 F⁽²³⁾

Furnace oxidation tests: specimens cycled to room temperature about once each hour. Average of three specimens reported.

area. All the coatings passed the 1- and 2-hour cyclic plasma-arc tests at 2000 and 2500 F, respectively, except the Chromalloy and AMF coatings which developed pin holes at 2500 F. The Vitro coating was not tested.

All as-coated specimens passed the 90-degree 4T bend test at room temperature with the exception of those coated by AMF. Bend ductility of some systems decreased after oxidation exposure at 2000 and 2500 F as shown in Table 28, although some ductility was retained by all specimens. Tensile-test results are shown in Figure 32 in comparison to initial substrate values. The original foil thickness was used for calculating strength values. Elongation was reduced considerably by all coatings; this may account for lower retained ultimate strength relative to the yield strength (because of reduced strain hardening).

The over-all performance of the coatings applied by Vought, GT & E, Pfaunder, and Chromalloy was considered better than that of the others, so they were selected for advanced evaluation in a program that is currently under way.

Oxidation Performance of Silicide Coatings at Low Pressures⁽³⁴⁾

Lockheed has investigated the oxidation protection afforded by silicide coatings on molybdenum at low oxygen pressures to gain some information about the capabilities of the coatings for resisting failure during re-entry. Coated molybdenum rods were resistance heated in a vacuum chamber. Oxygen pressure was controlled by balancing an oxygen leak against the vacuum pump. Specimens were exposed at a given oxygen pressure and temperature for 30 minutes.

The maximum temperatures for 30 minutes' life for the four coatings tested are shown in Figure 33. The Disil II, PFR-6, and Durak-B coatings suffered a reduction of about 450 F in their 30-minute life at 0.2 mm oxygen pressure in comparison to 760 mm air pressure. The Chance Vought coating, which is more limited in maximum temperature capability at atmospheric pressure, was actually superior to the other coatings in these tests as it did not show the extreme sensitivity to low-pressure deterioration.

The coatings failed in the low-pressure tests by localized attack at coating cracks, causing substrate oxidation. A gaseous oxidation product that condensed on the furnace walls was found to be amorphous and rich in silicon. This gaseous transport of silicon plus thermodynamic considerations has led Lockheed to believe that the failure mechanism for the silicide coatings at reduced pressure involves stabilization and volatilization of SiO.

Oxidation Tests of Silicide Coatings on Mo-0.5Ti⁽³⁵⁾

The University of Dayton has reported on the oxidation performance of five silicide coatings on 30-mil Mo-0.5Ti sheet in the following tests:

- (1) Coating life at 3000 F - specimens heated at 3000 F with oxyacetylene or plasma-arc torch

TABLE 28. ROOM-TEMPERATURE BEND TESTS OF COATED TZM FOIL IN AS-COATED CONDITION AND AFTER OXIDATION EXPOSURE^{(a)(23)}

Coating	Bend Angle in As-Coated Condition, degrees	Bend Angle After Oxidation Exposure at Indicated Temperature			
		2000 F		2500 F	
		Oxidation Time, hr	Bend Angle, degrees	Oxidation Time, hr	Bend Angle, degrees
Bare substrate	90, 90	--	---	--	--
Chromizing	90, 90	9	30, 90, 20	5	68, 90, 90
Vought	90, 90	38	90, 19, 15	18	80, 72, 76
GT&E	90, 90	15	90, 90, 90	2	90, 90, 90
GTC	90, 90	--	--	--	--
Pfautler	90, 90	30	19, 90, 21	7	90, 90, 90
Chromalloy	90, 90	36	12, 22, 21	3	19, 90, 79
AMF	19, 19	--	--	--	--
Vitro	90, 90	35	90, 90, 90	50	31, 34, 40

(a) Test procedure:

- (1) Specimens preoxidized in static furnace exposure (no cycling) for about 85 per cent of the cyclic life of the coating system.
- (2) Bend radius = 0.024, nominal at bend radius. Tested according to procedure recommended by the Refractory Metals Sheet Rolling Panel of MAB. Bend angle is that angle at which fracture occurred, or 90 degrees if specimen did not fracture.

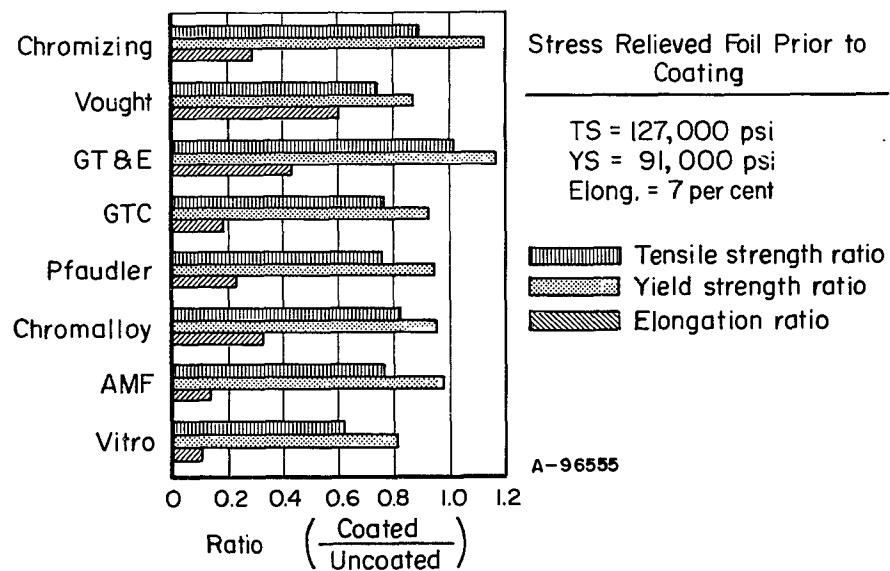


FIGURE 32. ROOM-TEMPERATURE TENSILE PROPERTIES OF AS-COATED TZM FOIL

Strength values based on foil thickness prior to coating.⁽²³⁾

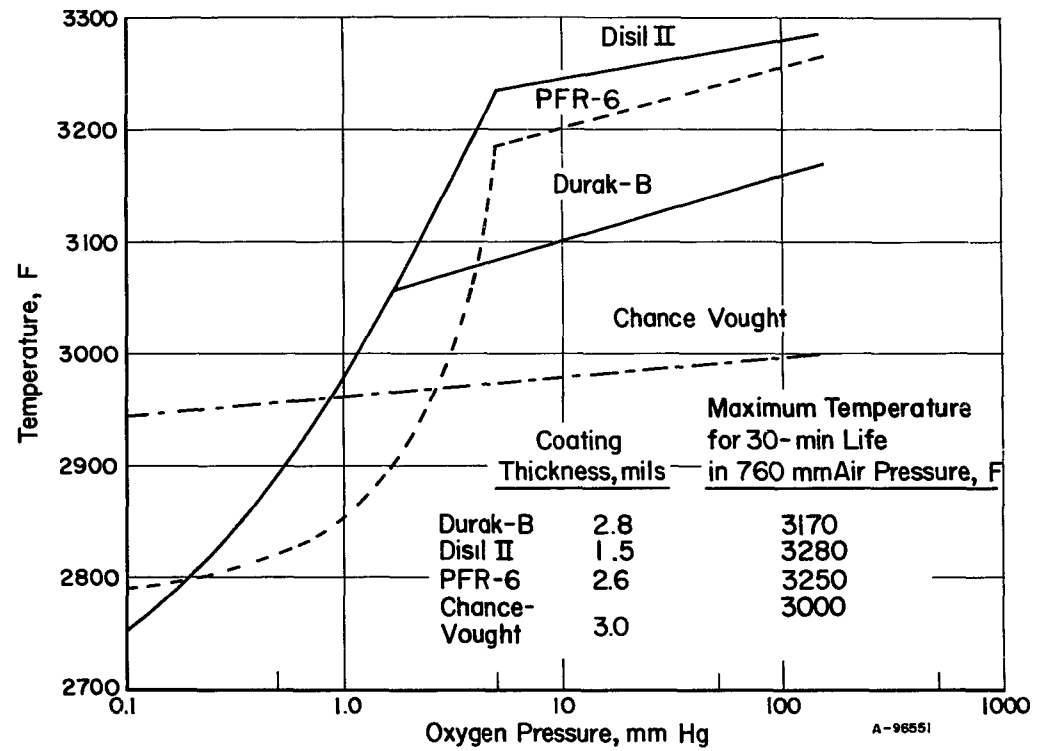


FIGURE 33. MAXIMUM TEMPERATURE FOR 30-MINUTE LIFE OF COATINGS ON MOLYBDENUM IN PURE OXYGEN ATMOSPHERE⁽³⁴⁾

- (2) Maximum useful temperature - specimens heated for consecutive 5-minute periods at 2500, 2700, 2900, 3000, 3100, 3200, 3300, and 3400 F, or until coating failure
- (3) Check for pest occurrence - specimens exposed for 50 hours at 2000 F*

The test results are given in Table 29. Coating lines were erratic in the plasma-arc test at 3000 F, but they were fairly uniform for duplicate specimens in the oxyacetylene-torch test. The PFR-6 coating displayed the best over-all performance; its oxidation life at 3000 F varied from 1 to more than 4 hours, and it had a maximum temperature capability of 3400 F. None of the coatings failed by the pest phenomenon at 2000 F.

TABLE 29. OXIDATION PERFORMANCE OF COATED 30-MIL Mo-0.5Ti SHEET^{(a)(35)}

Coating	3000 F Oxyacetylene- Torch-Test ^(b) Coating Life, min	3000 F Plasma-Arc Torch-Test ^(c,d) Coating Life, min	Plasma-Arc Test at Increasing Temperatures ^(d,e)			Coating Performance in 50 Hr, 2000 F, Furnace Oxidation Test
			Coating Failure Temperature, F	Total Exposure Time, min	Time at Failure Temperature, min	
Boeing Fluidized Bed Silicide	--	223, 90	3300	32	2	Edge failure at 25 hours; no pest
			3300	34	4	
Boeing Disil 1	22, 24, 25	2, 105	3300	34	4	Good; no pest
			3400	37	2	
PFR-6	64, 66, 82	>240, >240	3400	35	<1	Good; no pest
			3400	39	4	
W-2	21, 24, 25	25, >240	3200	26	1	Good; no pest
			3200	29	4	
Vought II & IV	60, 67, 84	28, 96	3200	26	1	Good; no pest
			3300	31	1	

(a) Test specimens were 2 by 2-inch sheet.

(b) Specimens cooled to room temperature once each 30 minutes.

(c) Specimens cooled to room temperature once each 15 minutes.

(d) Arc effluent was simulated air at a mass flow rate of 0.0082 lb/sec.

(e) Each specimen exposed for consecutive 5-minute periods at 2500, 2700, 2900, 3000, 3100, 3200, 3300, and 3400 F, or until coating failed.

Dynamic Oxidation Tests of Durak-MG and W-2 Coatings⁽³⁶⁾

Simulated leading-edge components (Figure 34) of Mo-0.5Ti alloy machined from solid stock and coated with W-2 and Durak-MG have been tested in a dynamic air environment by NASA. One test facility was a 6-inch subsonic arc-powered tunnel

*2000 F is above the temperature range in which pest has been reported to occur in MoSi₂. No reason for selection of this temperature was given.

operated at a reduced air pressure of 2 psi. The other test facility was a subsonic arc jet operating in the open atmosphere with the effluent consisting of air plus CO and CO₂ from the carbon electrodes. Surface temperature of the leading-edge specimens was 3000 F during the tests.

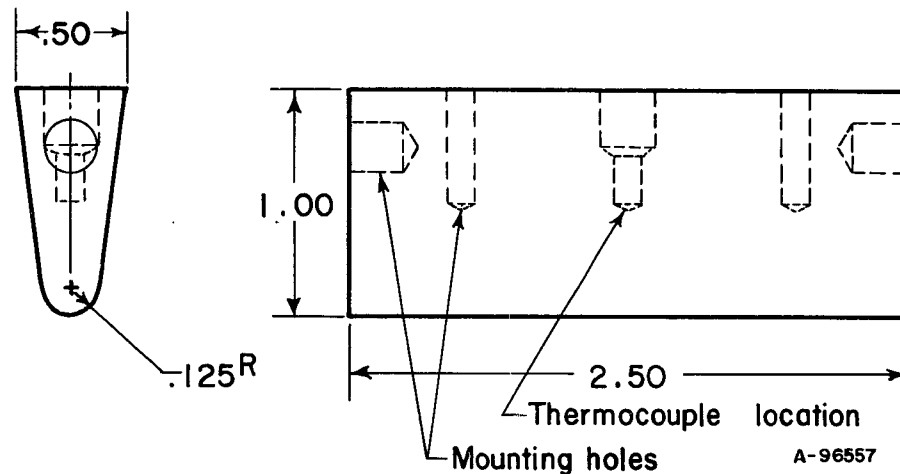


FIGURE 34. DESIGN OF COATED Mo-0.5Ti LEADING-EDGE SPECIMEN⁽³⁶⁾

The test results are summarized in Table 30. Both coatings protected the substrate from oxidation for the duration of the tests, which lasted 70 seconds in the low-pressure tunnel and 5 and 10 minutes in the atmospheric-pressure jet. Weight changes of the specimens were fairly low, ranging from -6 to +4 mg/cm², except for 20 mg/cm² gained by one specimen coated with W-2.

Tensile-Shear Tests of Coated Riveted Mo-0.5Ti Sheet^(37, 38)

Bell Aerosystems Company has conducted tensile shear tests of riveted Mo-0.5Ti sheet specimens coated with Durak-B and W-2 silicide coatings. Stress-relieved sheet specimens (10, 30, and 50 mils thick) and rivets were coated, and then the test specimens (Figure 35) were riveted at about 1500 F. Finally, the assembled test specimens were coated again. Prior to tensile testing the specimens were subjected to various pretreatments consisting of oxidation exposure at 2000 and 2500 F and low tensile loads (considerably below the elastic limit) at room temperature and 2500 F. These treatments are described in the footnotes in Table 31. The oxidation exposures at 2500 F recrystallized the Mo-0.5Ti and rivets.

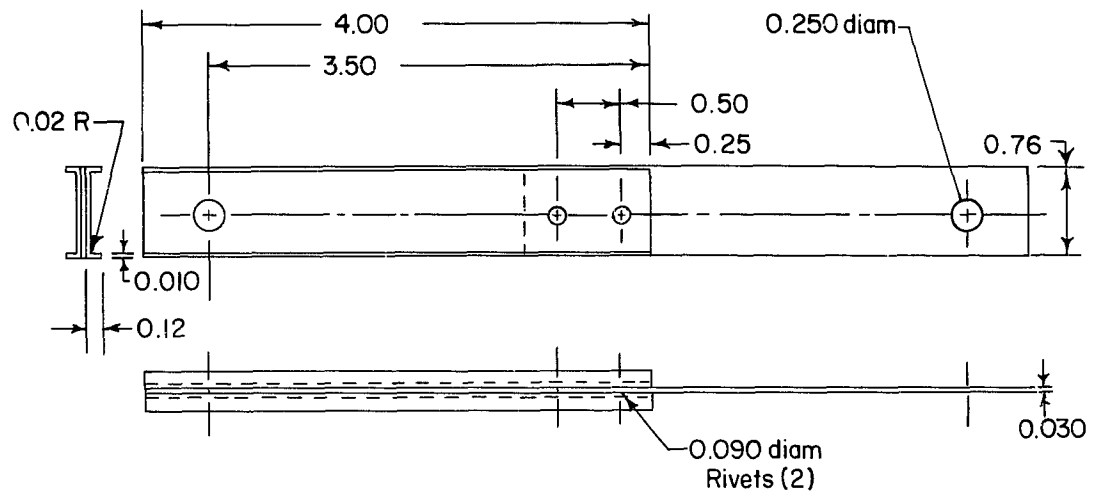
The tensile-shear strengths of the coated specimens are compared with calculated failure loads for uncoated specimens in Table 31. With only a few exceptions the strengths of the coated specimens were in fair agreement with the values that were calculated for uncoated specimens.

TABLE 30. TEST DATA FOR COATED Mo-0.5Ti LEADING-EDGE SPECIMENS TESTED BY NASA IN TWO ARC-POWERED FACILITIES⁽³⁶⁾

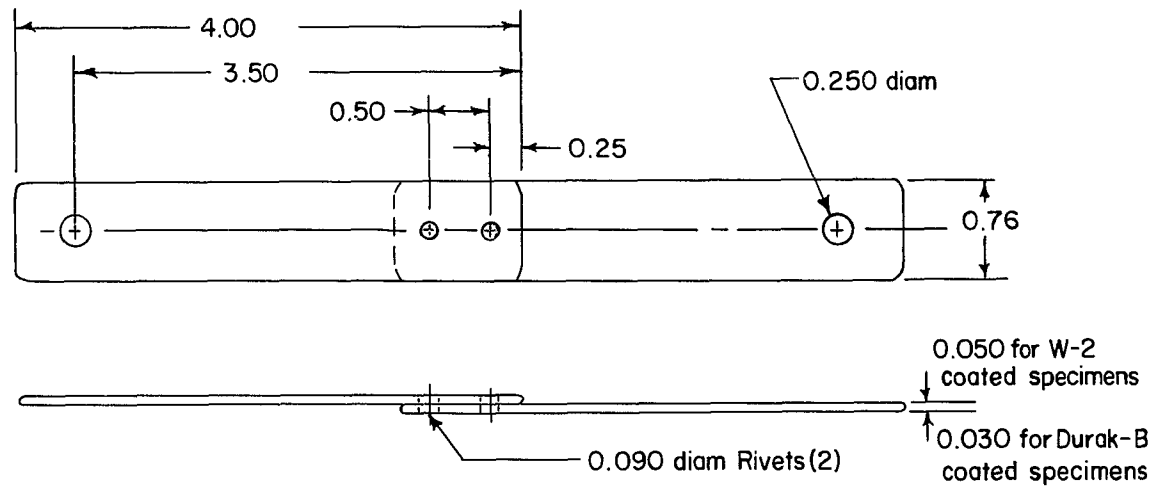
Coating	Test Time, min	Characteristics of Test Facility (a)			Surface Temperature, F	Weight Change of Specimen, mg/cm ²
		Air Flow, lb/sec	Heat Input Btu/ft ² -sec	Static Pressure, psia		
Tests Conducted With Arc Jet						
W-2	5.0	0.24	210	14.7	3000	+3.4
Durak MG	2.4	0.24	210	14.7	3000	+0.2
Durak MG	5.0	0.24	210	14.7	3000	-0.8
W-2	10.0	0.08	170	14.7	3000	+20.0
Durak MG	9.5	0.08	170	14.7	3000	-5.8
Tests Conducted in Low-Pressure Arc-Powered Tunnel						
W-2	1.16	0.08	220	2	3000	+1.0
Durak MG	1.16	0.08	220	2	3000	+0.4

(a) Additional characteristics of test facilities used for these tests:

	6-Inch Subsonic Low-Pressure Arc-Powered Tunnel	Subsonic Arc Jet
Test Section Diameter, in.	6	6
Test Atmosphere	2-psia air	Air + 4% carbon as CO and CO ₂ from carbon electrodes
Stagnation Temperature, F	7200	3200-8500 (two values refer to low- and high-arc-power tests)
Enthalpy, Btu/lb	3900	1000-4500
Velocity, ft/sec	720	40-300
Dynamic Pressure, lb/ft ²	4.7	0.25-6.0
Mach Number	0.17	0.01-0.06
Reynolds Number Per Foot	6,500	6,000 to 30,000



a. Double Shear Specimen



A-96543

b. Single Shear Specimen

FIGURE 35. CONFIGURATION OF COATED RIVETED Mo-0.5Ti SHEET SPECIMENS⁽³⁷⁾

All dimensions are in inches.

TABLE 31. TENSILE-SHEAR STRENGTH OF COATED RIVETED Mo-0.5Ti SPECIMENS TESTED IN AIR^(37, 38)

Type Specimen(a)	Prior History(b)	Test Temperature, F	Failure Load ^(c) , pounds	Failure Location	Calculated Failure Load ^(d) , pounds
<u>Specimens Coated With W-2</u>					
Double shear	A	RT	564-1020 (836)	1/4-inch loading-pin holes	800
Single shear	A	RT	925-1065 (973)	Rivets and base metal	935-1470
Double shear	B	RT	406-673 (517)	Base metal at rivets	540
Single shear	C	RT	935-1020 (970)	Rivets sheared	625
Double shear	B	2500	190-297 (235)	Base metal at rivets	135
Single shear	C	2500	200-253 (228)	Rivets sheared	155
<u>Specimens Coated With Durak-B</u>					
Double shear	A	RT	440-546 (493)	1/4-inch loading-pin holes	800
Single shear	A	RT	785-1005 (895)	Rivets and sheet adjacent to rivets	880-935
Double shear	B	RT	465-520 (496)	Base metal at rivets	540
Single shear	C	RT	725-850 (785)	Rivets sheared	625
Double shear	A	2500	180-215 (198)	Base metal at rivets	135
Single shear	A	2500	190-200 (195)	Rivets sheared	155
Double shear	B	2500	215-229 (222)	Base metal at rivets	135
Single shear	C	2500	195-213 (205)	Rivets sheared	155

Footnotes appear on the following page.

Footnotes for Table 31:

(a) See specimen designs in Figure 38.

(b) Prior history of test specimens:

A = Oxidized in air for 10 minutes at 2000 F

B = A + cyclic load of 115 to 210 pounds applied 10 times at room temperature; followed by heating in air at 2500 F for 4 minutes under a 6.5-pound load

C = A + cyclic load of 290 to 315 pounds applied 10 times at room temperature; followed by heating in air at 2500 F for 4 minutes under 16-pound load.

(c) Failure load range is followed by average value in parentheses where applicable.

(d) Calculated failure loads:

	Calculated Failure Load for Uncoated Material, pounds		
	at 80 F for	at 80 F for	at 2500 F for
	As-Received Material	Recrystallized Material	Recrystallized Material
2 rivets, 0.090-inch diameter			
Single shear	935	625	155
Double shear	1870	1250	310
2 channels 0.010 inch thick			
Loading-pin hole (stress-concentration factor of 2.25 assumed)	800	535	--
Rivet hole, tension (stress-concentration factor of 2.70 assumed)	810	540	135
Rivet hole, bearing	765	510	125
1 sheet 0.050 inch thick			
Loading-pin hole	1330	885	--
Rivet hole, tension	1470	980	245
Rivet hole, bearing	1910	1270	320
1 sheet 0.030 inch thick; rivet hole, tension	880	590	--

Tensile and Fatigue Tests of Coated
Threaded Fasteners⁽³⁹⁾

Republic Aviation is engaged in a program to design and manufacture refractory-metal fasteners that can be used in the coated condition. Bolts having a rounded thread form for the root and crest have been made in the 1/4-20 size from TZC and TZM molybdenum alloys. The limited amount of test data available for these fasteners is a premonition of some of the problems that can be anticipated with other coated refractory-metal threaded fasteners.

The tensile-failure loads of the uncoated and coated 1/4-20 TZC and TZM fasteners are given in Table 32. Room-temperature failure loads were reduced 50 to 70 per cent by the PFR-6 and W-3 coatings, but only 20 per cent by the Vitro coating. Bolts coated with PFR-6 and W-3 had higher strength at 2000 F than at room temperature, suggesting increased notch sensitivity effected by the coating. TZM as the substrate was somewhat superior to TZC at both test temperatures.

TABLE 32. TENSION-FAILURE LOADS OF COATED 1/4-20 TZC AND TZM BOLTS
AT ROOM TEMPERATURE AND 2000 F⁽³⁹⁾

Condition	Test Temperature, F	Failure Load, pounds ^(a)
<u>TZC Bolts</u>		
Uncoated	RT	4440-4595 (4528)
Coated with PFR-6	RT	950-1850 (1312)
Ditto	2000	2595 (2595)
Coated with W-3	RT	1550-1820 (1685)
Ditto	2000	2200
Coated with Vitro	RT ^(b)	3245-3965 (3605)
94MoSi ₂ -6Ni	RT	2565
Ditto	2000	2500
<u>TZM Bolts</u>		
Uncoated	RT	4850-5340 (5072)
Coated with PFR-6	RT	1560-2725 (2111)
Ditto	2000	2830-2840 (2835)
Coated with W-3	RT	2860
Ditto	2000	3010

(a) Range is followed by average in parentheses where more than 1 specimen was tested.

(b) Specimens previously oxidized for 24 hours at 2500 F.

PFR-6 is the only coating for which fatigue data are available at this time. The tension-tension fatigue lives of PFR-6 coated bolts at room temperature are given in Table 33. The fatigue life of the bolts dropped precipitously upon being coated. In

TABLE 33. RESULTS OF ROOM-TEMPERATURE TENSION-TENSION FATIGUE TESTS OF
1/4-20 TZC AND TZM BOLTS⁽³⁹⁾

Maximum Tensile Load, pounds ^(a)	Cycles to Failure	Failure Location ^(b)
<u>Uncoated TZC</u>		
3400	9,000	Threads
3400	24,000	"
2945	57,000	"
2945	18,000	"
2265	2,000,000	No failure
2265	2,000,000	No failure
<u>PFR-6-Coated TZC^(c)</u>		
1200	2,000	Head
1200	320,000	Threads
1200	--	Broke on loading; threads
1000	--	Broke on loading; head
1000	112,000	Head
975	1,258,000	Threads
975	1,000	Head
975	38,000	Head
800	2,000,000	No failure
800	2,000,000	No failure
800	4,000	Head
800	6,000	Head
800	2,000,000	No failure
750	16,000	Head
750	12,000,000	No failure
400	2,000,000	No failure
<u>Uncoated TZM</u>		
2945	434,000	Threads
2945	1,953,000	Threads
2945	622,000	Threads
<u>PFR-6-Coated TZM^(c)</u>		
1800	--	Broke on loading; threads (two specimens)
1700	496,000	Head
1600	417,000	Threads
1600	400,000	No failure
1500	240,000	Head
1500	--	Broke on loading
1500	322,000	Threads
1500	1,500,000	Threads

(a) Ratio of minimum load to maximum load was 0.1.

(b) Threads = failed in threads; head = failed in head-to-shank fillet radius.

(c) PFR-6 coating applied by Republic with technique recommended by Pfadler.

addition, the fatigue life of coated bolts under a given load was erratic. The maximum tensile load for 2 million cycles' life with TZC bolts was 2200 pounds for uncoated specimens, but only 800 pounds for coated bolts. Yet three coated bolts tested at 750 or 800 pounds' load failed in less than 20,000 cycles, two orders of magnitude below the maximum fatigue life at this load. The fatigue life of a coated TZC bolt at 2000 F was 515,000 cycles under 1300 pounds' load, whereas the longest life at room temperature with a 1200-pound load was 312,000 cycles. TZM, both uncoated and coated, was superior to the TZC alloy.

Apparently the presence of a coating such as PFR-6 or W-3 and the notched-thread form synergistically embrittle the bolts at room temperature.

Emittance of Silicide Coatings

Emittance data obtained by several investigators for silicide coatings on molybdenum or molybdenum alloys are summarized in Table 34 and Figures 36 to 40. The spectral normal emittance (0.65μ) and the total normal emittance of the PFR-6 coating in a vacuum were above 0.80 (Table 33), and the total hemispherical emittance in air varied between 0.6 and 0.7 (Figure 36). The total hemispherical emittance of Durak-B coating in air ranged from 0.40 to 0.55 at temperatures up to 3200 F (Figure 37). The emittance of Boeing's straight silicide coating on TZM increased from about 0.65 to about 0.9 as temperature increased from 2200 to 2800 F (Figure 38). The total hemispherical emittance of Vought IV coating varied from 0.6 to 0.7 at temperatures up to 3000 F (Figure 39). The spectral normal emittance of AMFKOTE-2 and AMFKOTE-2 which was modified to improve its emittance is compared with that of bulk MoSi_2 in Figure 40. Emittances of the standard AMFKOTE-2 and MoSi_2 are similar, but the modified coating exhibits higher emittance.

COATINGS FOR TANTALUM AND TANTALUM-BASE ALLOYS

Activity in developing and testing coatings for tantalum and its alloys is not nearly so extensive as it is for columbium and molybdenum alloys. The tantalum alloys for which advanced experimental coatings are available are Ta-10W and Ta-30Cb-7.5V. The performance of the GT & E tin-aluminum coatings on Ta-10W and Ta-30Cb-7.5V and the Battelle straight silicide coating on Ta-30Cb-7.5V alloy has been well characterized with regard to oxidation performance at atmospheric pressure and mechanical properties. Information is lacking on the emittance of both coating systems and low-pressure oxidation performance of the silicide coating system.

General Telephone & Electronics Tin-Aluminum Coatings⁽¹⁷⁾

The family of tin-aluminum coatings developed for tantalum alloys by General Telephone and Electronics (GT & E) has undergone a transition in their chemical composition within the past 2 years to provide better over-all performance. The earlier coatings had compositions prior to sintering of Sn-25Al (designated 40S) or Sn-50Al

TABLE 34. EMITTANCE OF PFR-6 COATING ON MOLYBDENUM IN A VACUUM

Temperature, F	Spectral Normal Emittance (0.65 μ)(40)
1449	0.98
1674	0.95
1679	0.92
1920	0.93
1920	0.92
2066	0.91
2071	0.88
2242	0.88
2248	0.89
2584	0.82
2601	0.79
Temperature, F	Total Normal Emittance(41)
1562	0.88
1742	0.84
1922	0.83
2102	0.83
2282	0.84
2462	0.85
2642	0.89
2822	0.93
3002	0.96

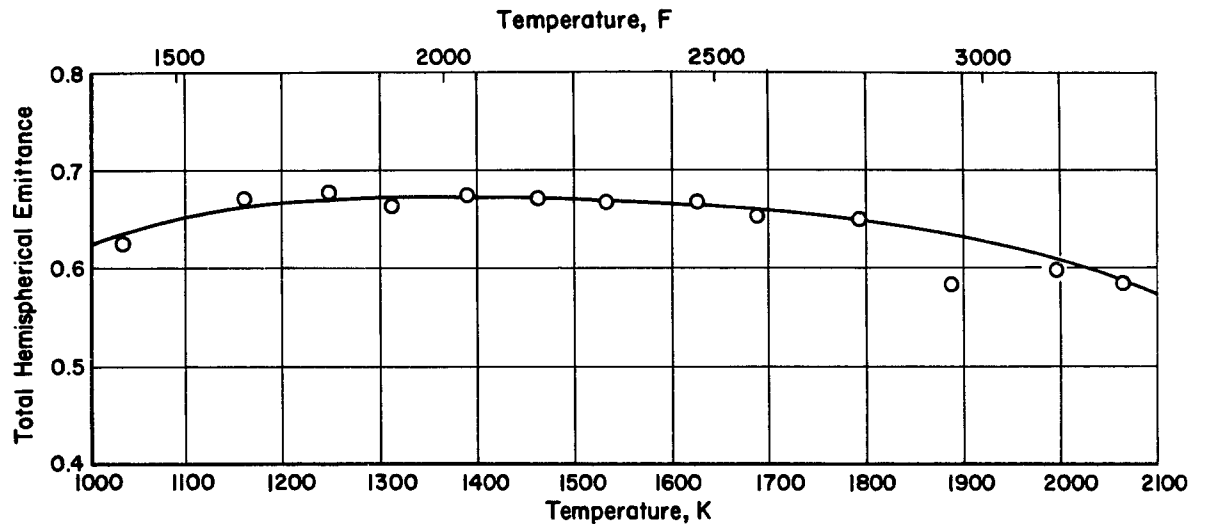


FIGURE 36. TOTAL HEMISPHERICAL EMITTANCE OF PFR-6 COATING ON MOLYBDENUM MEASURED IN AIR⁽⁹⁾

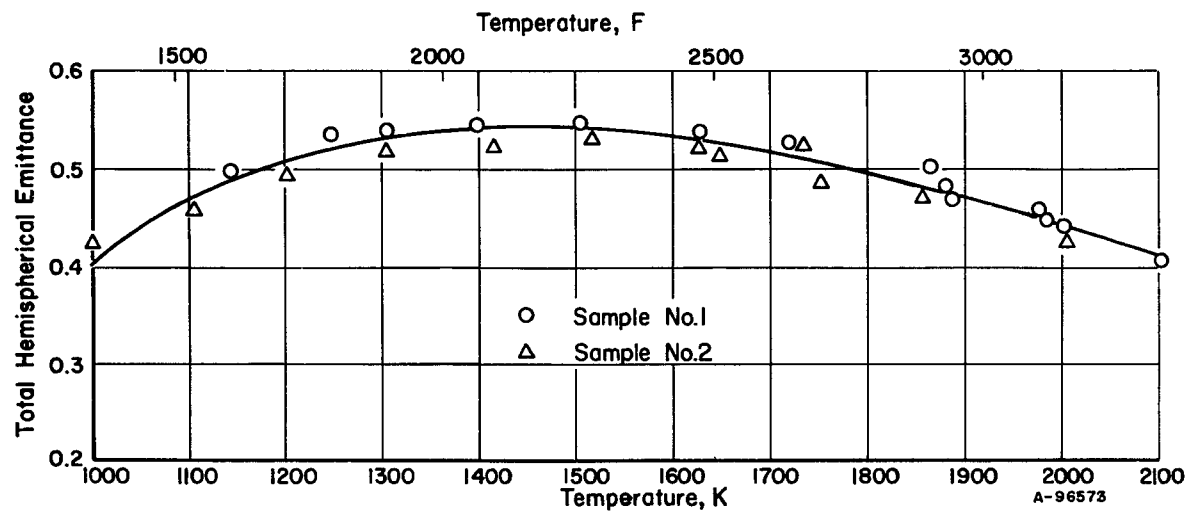


FIGURE 37. TOTAL HEMISPHERICAL EMITTANCE OF DURAK-B COATING ON MOLYBDENUM IN AIR⁽⁹⁾

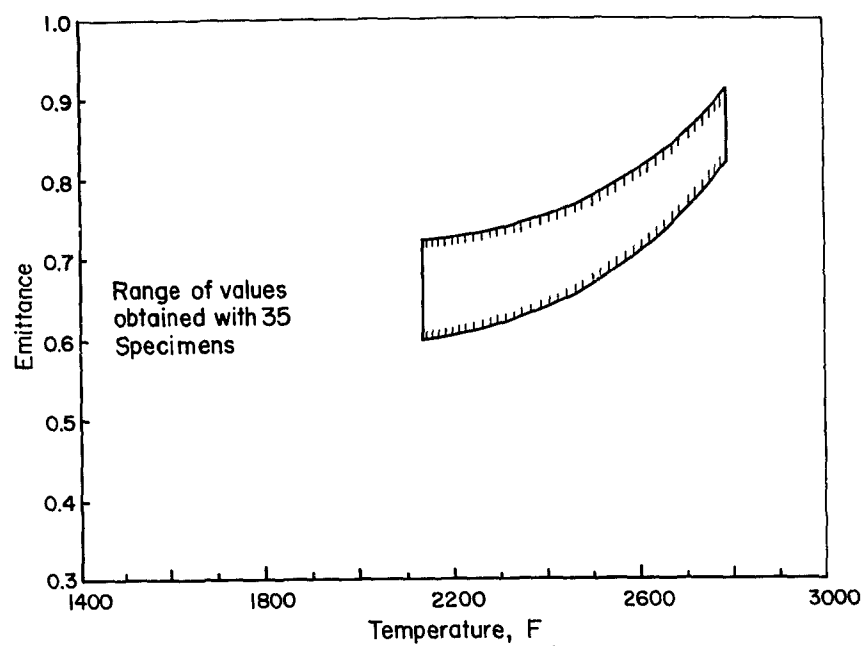


FIGURE 38. EMITTANCE OF BOEING'S STRAIGHT SILICIDE COATING ON TZM ALLOY⁽⁵⁾

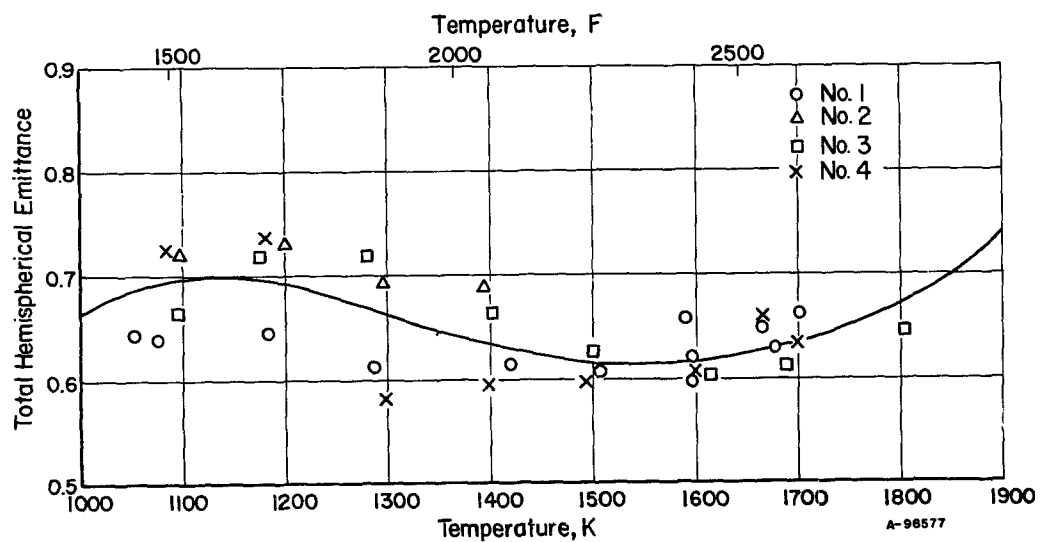


FIGURE 39. TOTAL HEMISPHERICAL EMITTANCE OF VUGHT IV COATING ON MOLYBDENUM IN AIR⁽⁹⁾

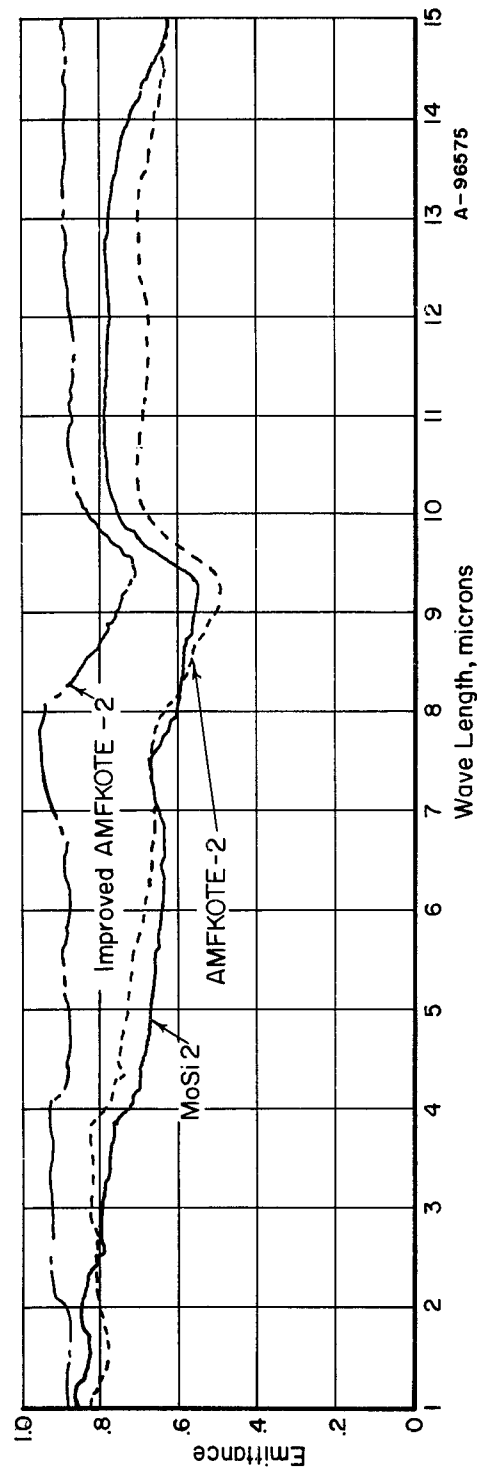


FIGURE 40. SPECTRAL NORMAL EMITTANCE OF A SINTERED SAMPLE OF MoSi₂ AND AMFKOTE-2 COATING ON MOLYBDENUM AT 1832 F(42, 43)

(34S). A distracting feature of these first-generation coatings was that a lump of Sn-Al formed at the drain-off end of specimens during the sintering heat treatments. Retention of the lump resulted in excessive diffusion interaction of the lump with the substrate during service, and its removal resulted in reduced oxidation life. The problem was minimized by adding a refractory powder such as tantalum or molybdenum to the slurry to support the coating during sintering and thereby prevent runoff.

GT & E has conducted extensive evaluations of the following substrate-coating systems:

Substrate	Applied Coating Composition, weight per cent
Ta-10W	(Sn-25Al)-10TaAl ₃
Ta-10W	(Sn-50Al)-10TaAl ₃
Ta-10W	(Sn-25Al)-10MoAl ₃
Ta-30Cb-7.5V	[Sn-50(Al-11Si)]-10TaAl ₃ , identified hereafter as (Sn-50Al-Si)-10TaAl ₃
Ta-30Cb-7.5V	[Sn-50(Al-11Si)]-10MoAl ₃ , identified hereafter as (Sn-50Al-Si)-10MoAl ₃

To clarify the compositions, (Sn-25Al)-10TaAl₃ is 90 weight per cent (Sn-25Al) and 10 per cent TaAl₃. The elemental powders (Sn, Al, Ta, etc.) are mixed in a 1 to 1 volume ratio with lacquer. The slurry is sprayed on specimens, and then the specimens are dried and sintered in a vacuum for 1/2 hour at 1900 F. Thicker coatings are obtained by repeating the paint and sinter sequence a second time. The coatings range in thickness up to 6 mils. During sintering the molten aluminum reacts with the substrate and the tantalum or molybdenum powder in the coating to form MAl₃ aluminides. The unreacted Sn-Al phase is molten in service at temperatures above 1200 F.

Typical lives of the coatings in cyclic furnace oxidation tests are presented in Table 35 and Figure 41. Average coating life was 50 to 100 hours at temperatures up to 2000 F. At temperatures from 2500 to 3000 F, coating life increased with increasing coating thickness and length of oxidation cycle (Figure 41). For instance, oxidation life of the (Sn-25Al)-10MoAl₃ coating on Ta-10W at 2800 F was tripled by increasing the length of oxidation cycles from 1 to 12 hours. Doubling the coating thickness approximately doubled the oxidation life at 2500 F. The (Sn-25Al)-10TaAl₃ coating on Ta-10W resisted failure for 1 hour at 3300 F in oxyacetylene-torch tests.

Preliminary low-pressure oxidation tests indicated that the tin-aluminum coatings are susceptible to early failure due to volatilization of the liquid Sn-Al phase. About 70 weight per cent of a (Sn-25Al)-10TaAl₃ coating was lost in 30 minutes at 2600 F under 1.5 mm air pressure. The coating was depleted similarly in 1 hour at 2450 F. On the other hand, the coating was stable under 3 mm pressure at 2600 F and under 6 mm at 2800 F.

The tensile and stress-rupture properties of the coated alloys are shown in Figures 42 to 46. Figure 42 to 44 show similar tensile properties of coated and uncoated Ta-10W. The loss in strength depicted in Figure 44 resulting from oxidation at 2500 and 3000 F probably reflects both recrystallization and diffusion consumption of the

TABLE 35. OXIDATION LIVES OF Sn-Al COATINGS ON Ta-10W AND Ta-30Cb-7.5V ALLOYS^{(a)(17)}

Substrate	Coating	Oxidation Temperature, F	Coating Life, hr ^(b)
Ta-10W	(Sn-25Al)-10TaAl ₃	1100	21-162
Ta-10W	(Sn-50Al)-10TaAl ₃	1100	44-63
Ta-30Cb-7.5V	(Sn-50Al-Si)-10TaAl ₃	1100	>100
Ta-10W	(Sn-25Al)-10TaAl ₃	1400	23-157
Ta-30Cb-7.5V	(Sn-50Al-Si)-10TaAl ₃	1400	>100
Ta-10W	(Sn-25Al)-10TaAl ₃	2000	>100
Ta-10W	(Sn-50Al)-10TaAl ₃	2000	71-96
Ta-30Cb-7.5V	(Sn-50Al-Si)-10TaAl ₃	2000	>100
Ta-10W	(Sn-25Al)-10TaAl ₃	2500	16-77
Ta-30Cb-7.5V	(Sn-50Al-Si)-10TaAl ₃	2500	43-87
Ta-30Cb-7.5V	(Sn-50Al-Si)-10MoAl ₃	2500	>100
Ta-10W	(Sn-25Al)-10TaAl ₃	2800	3-15
Ta-10W	(Sn-25Al)-10MoAl ₃	2800	21-51
Ta-10W	(Sn-50Al)-10TaAl ₃	2800	6-7
Ta-30Cb-7.5V	(Sn-50Al-Si)-10TaAl ₃	2800	7-31
Ta-30Cb-7.5V	(Sn-50Al-Si)-10MoAl ₃	2800	24-40
Ta-10W	(Sn-25Al)-10TaAl ₃	3000	3-10

(a) Tests conducted in still air in a furnace. Specimens generally cycled to room temperature ten times each 24 hours at and below 2500 F, and once each hour above 2500 F.

(b) Range of coating lives obtained with coatings of varying thickness in multiple tests.

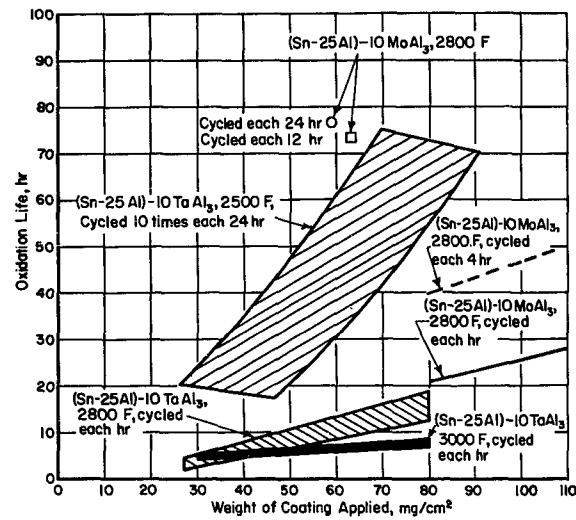


FIGURE 41. EFFECT OF COATING THICKNESS AND CYCLING ON LIFE OF (Sn-25Al)-10TaAl₃ AND (Sn-25Al)-10MoAl₃ COATINGS ON Ta-10W IN FURNACE OXIDATION TESTS⁽¹⁷⁾

25 mg/cm² = 2-mil coating; 90 mg/cm² = 5-mil coating.

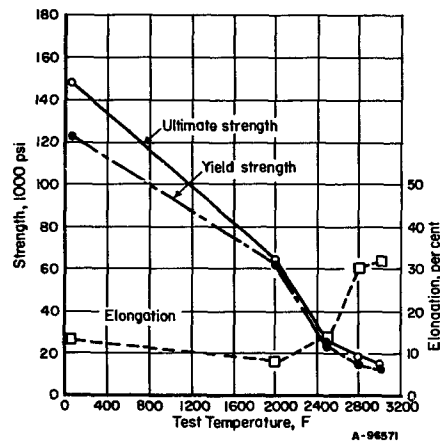


FIGURE 42. TENSILE PROPERTIES OF 40-MIL Ta-10W SHEET COATED WITH (Sn-25Al)-10TaAl₃, TESTED IN AIR⁽¹⁷⁾

Alloy apparently was in wrought or stress-relieved condition prior to coating.

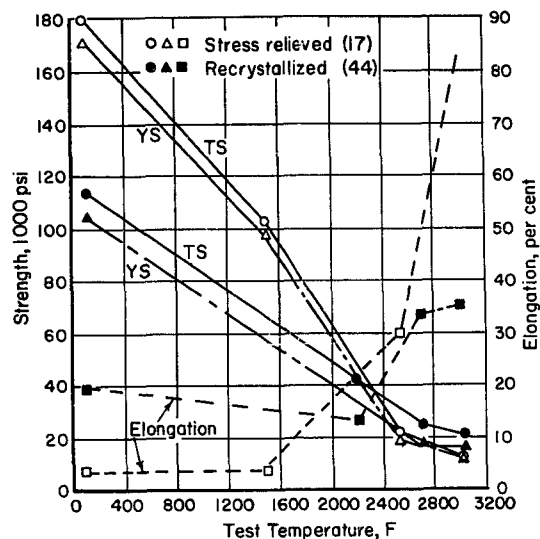


FIGURE 43. TENSILE PROPERTIES OF UNCOATED Ta-10W SHEET TESTED IN VACUUM

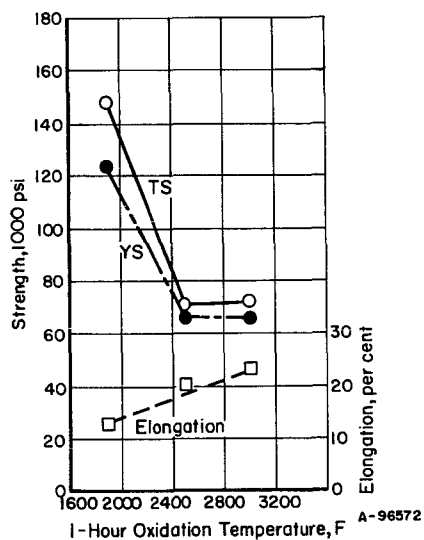
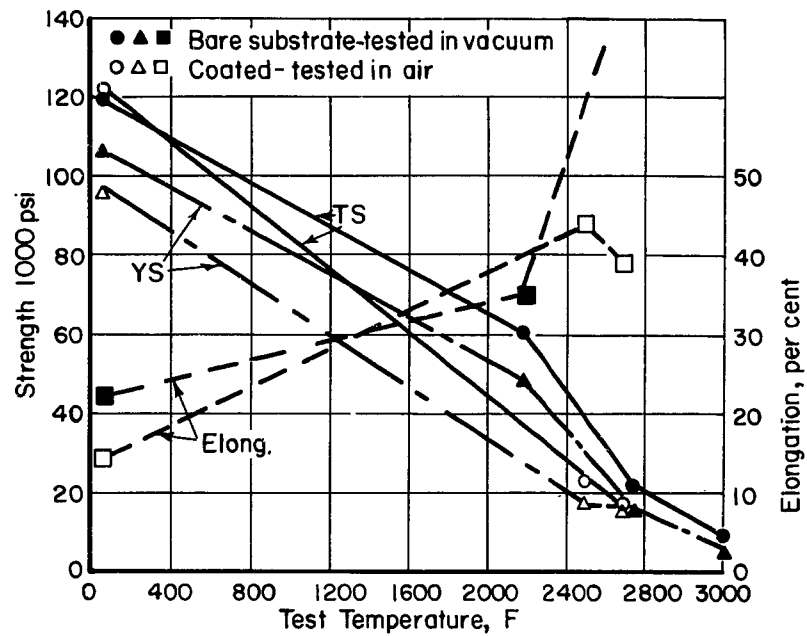
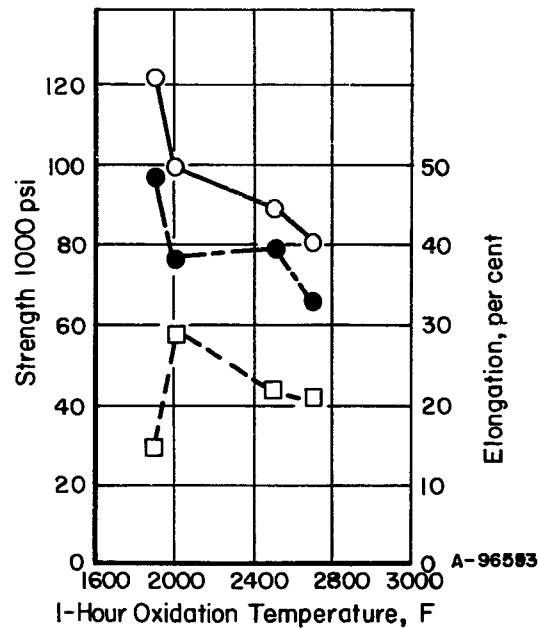


FIGURE 44. ROOM-TEMPERATURE TENSILE PROPERTIES OF Ta-10W SHEET COATED WITH (Sn-25Al)-10TaAl₃ AFTER OXIDATION FOR 1 HOUR AT VARIOUS TEMPERATURES

Alloy apparently was in the wrought or stress-relieved condition prior to coating.



a. Tensile Properties of Bare (Recrystallized) and Coated Ta-30Cb-7.5V at Various Temperatures



b. Room-Temperature Tensile Properties After Oxidation for 1 Hr at Various Temperatures

FIGURE 45. TENSILE BEHAVIOR OF (Sn-50Al-Si)-10TaAl₃-COATED Ta-30Cb-7.5V SHEET(17,44)

substrate during the oxidation exposure. Obviously, these effects are not embrittling. Figure 45 shows tensile properties and thermal stability for the coated Ta-30Cb-7.5V alloy. Coating weakens the alloy to some extent and the diffusion-consumption-weakening effect of the oxidation exposure may be somewhat more severe than for the Ta-10W alloy (recrystallization was not a factor in the loss of strength of the Ta-30Cb-7.5V alloy; it was recrystallized prior to coating). Figure 46 shows that the Sn-Al coating does not significantly degrade the rupture strength of Ta-10W in times to 6 hours at 2800 F or 2 hours at 3000 F. Because of lack of baseline data, the situation is uncertain for the coated Ta-30Cb-7.5V alloy.

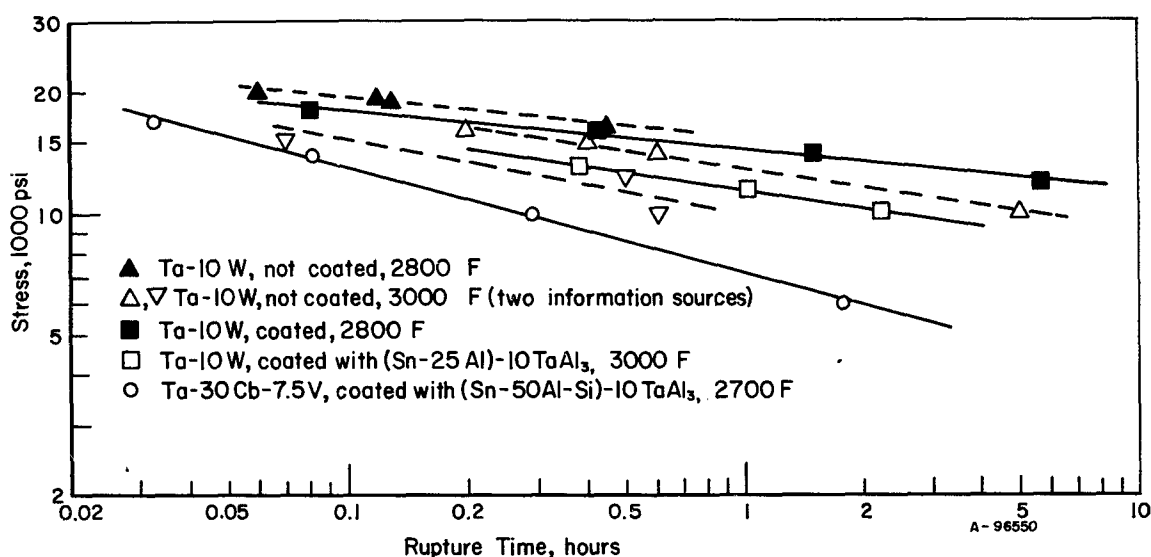


FIGURE 46. STRESS-RUPTURE CURVES FOR COATED AND UNCOATED Ta-10W AND Ta-30Cb-7.5V⁽¹⁷⁾

Coated specimens tested in air. Uncoated specimens tested in vacuum.

Results of cyclic and noncyclic plasma-arc oxidation tests conducted by the University of Dayton on 2 by 2-inch sheet specimens of Ta-10W protected by the Sn-50Al coating are given in Table 36. Specimens were heated in noncyclic tests for 5-minute intervals at progressively increasing temperatures. The cyclic tests consisted of heating specimens for 30 seconds and cooling in 10 seconds; specimens were cycled 15 times at each of several increasing temperatures. The maximum temperature at which the coating was protective was in excess of 3200 to 3300 F in the noncyclic tests, but was generally limited to about 2900 F in the cyclic tests. This difference may not be due to cycling alone, as prefailure chronotherms were different in the two tests.

TABLE 36. PERFORMANCE OF Sn-50Al COATING ON Ta-10W SHEET IN PLASMA-ARC OXIDATION TESTS⁽³⁵⁾

<u>Noncyclic Tests at Progressively Increasing Temperatures</u>			
	<u>Maximum Surface Temperature, F</u>	<u>Time at Temperature, min</u>	<u>Remarks</u>
Specimen 1	2070	5	
	2240	5	
	2530	5	
	2910	5	
	3230	5	Specimen warped, no failure
Specimen 3	2550	5	
	2910	5	
	3260	5	
	3340	5	No failure
<u>Cyclic Tests^(a)</u>			
	<u>Maximum Surface Temperature, F</u>	<u>Number of Cycles</u>	<u>Remarks</u>
Specimen 4	2730	15	
	2930	15	
	3150	4	Coating failed
Specimen 5	2740	15	
	2910	4	Coating failed
Specimen 6	2730	15	
	2910	11	Coating failed
Specimen 7	2730	15	
	2930	5	Coating failed
Specimen 8	2740	15	
	2910	8	Coating failed

(a) Specimens heated for 30 seconds and cooled for 10 seconds; 15 cycles at each test temperature.

Straight Silicide Coating on Ta-30Cb-7.5V Alloy⁽⁴⁵⁾

An investigation of the performance of straight silicide coatings on tantalum alloys at Battelle has established that pack-siliconized Ta-30Cb-7.5V alloy exhibits good oxidation resistance and mechanical properties. The silicide coating is applied by pack cementation under argon in a pack consisting of 17 weight per cent silicon powder, 81 per cent particulate Al_2O_3 , and 2 per cent NaF. Specimens are coated for 4 hours at 2200 F, repacked in fresh mix, and coated again for 12 hours at 2200 F. The resulting coatings are 4 mils thick. The principal coating layer is single phase in the as-coated condition and has the following composition based on electron-microprobe analysis:

	<u>Atom Per Cent</u>
Tantalum	12
Columbium	11
Vanadium	4
Silicon	73

This corresponds to a pseudo-compound having the composition $MSi_{2.8}$, where M represents the Ta-30Cb-7.5V substrate composition. Hence the tantalum, columbium, and vanadium occur in the coating in the same proportions as they do in the substrate. The coating system has been evaluated using 40-mil Ta-30Cb-7.5V alloy sheet stock.

The weight gain of the coating in cyclic oxidation tests is presented in Figure 47 and Tables 37 and 38. Whereas straight silicide coatings on unalloyed tantalum, Ta-10W, and Ta-8W-2Hf, suffered rapid oxidation (sometimes referred to as "pest") at 1800 F in a few hours, this vanadium-modified coating resisted the anomalous failure for 100 hours. The system does appear to be susceptible to early failure (50 hours) at 2000 F, however. The improved resistance of the coating to failure in the critical 1800 F temperature range is attributed to vanadium modification of the silicide coating. Oxidation weight gains were low at all temperatures except 1800 and 2000 F, but substrate protection was good for about 50 hours at either temperature. Coating life ranged from 2 to 12 hours at 2700 F, from 6 to greater than 17 hours at 2900 F, and 1 to 2 hours in oxyacetylene-torch tests at 3000 F. The coating was unable to self-heal at 20-mil holes that were drilled through the coating to expose the substrate.

Bend ductility of oxidized specimens was 0T at room temperature which is the same as that of the uncoated substrate (Table 37). Tensile properties of recrystallized 40-mil Ta-30Cb-7.5V sheet in the uncoated, coated, and coated plus exposed conditions are given in Table 39. Strength was based on the residual substrate cross-sectional area after coating. The tensile properties were not altered significantly by the coating at room temperature. The notched tensile data show that the coated substrate is not notch sensitive. At 2200 F, coated specimens were considerably stronger than uncoated specimens; this was interpreted as reflecting a strength contribution of the coating.

TRW Cr-Ti-Si Coating⁽⁴⁶⁾

Thompson Ramo Wooldridge has applied its Cr-Ti-Si coating on tantalum using the process developed for columbium. The resulting coating protects the substrate from oxidation for 30 hours at 2700 to 2800 F.

R-506 Coating^(17,47,48)

General Telephone & Electronics has applied its R-506 titanium-modified silicide coating to tantalum and columbium alloys. The coating process consists of titanizing by vacuum pack cementation at 2200 F followed by siliconizing with an atmospheric-pressure pack-cementation process. Table 40 shows that R-506 protects Ta-10W and Ta-30Cb-7.5V alloys from oxidation for several hours at 2800 F, and that it has long life at 1800 F where rapid oxidation normally occurs in unmodified silicide coatings on Ta-10W alloy.

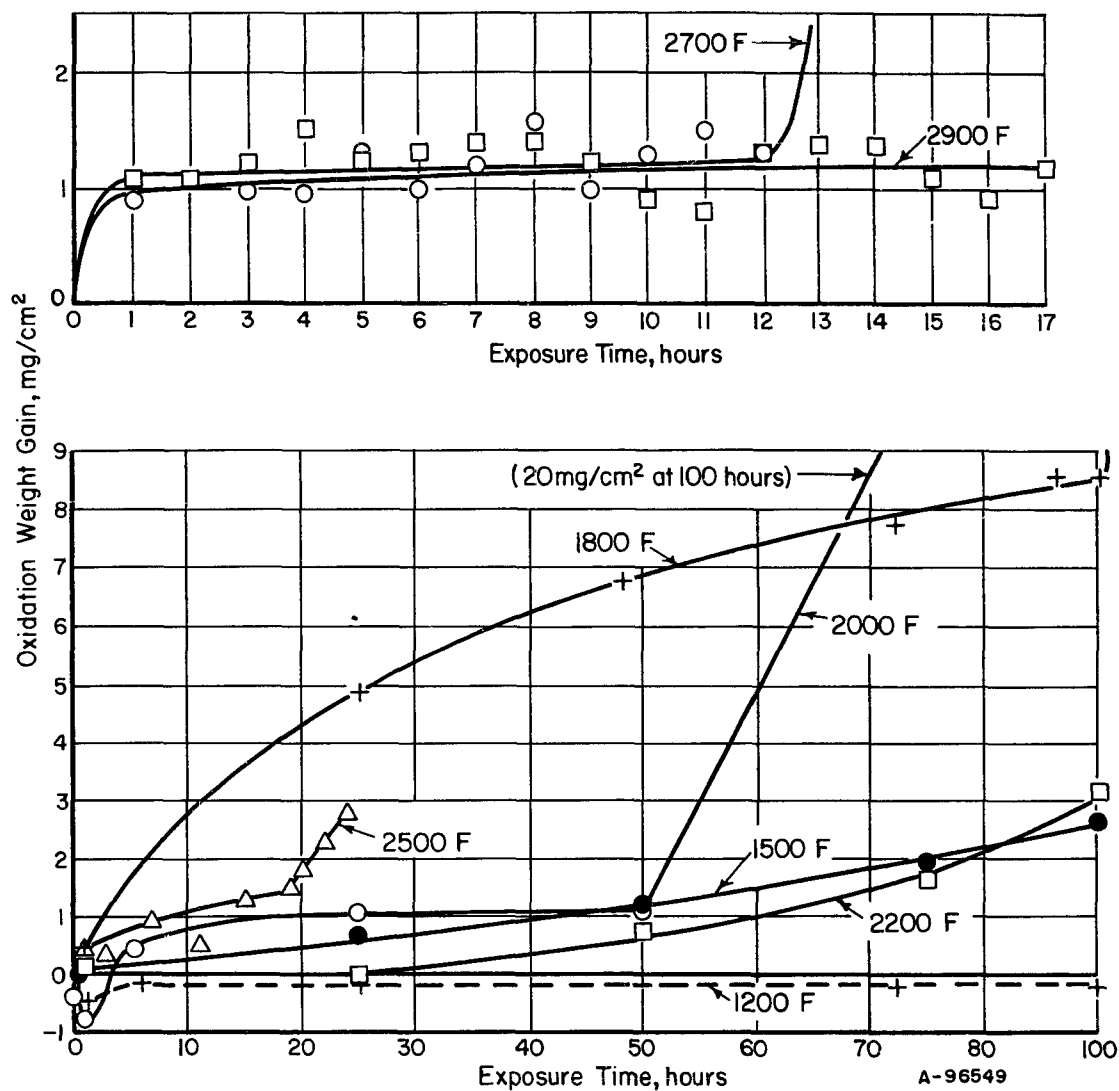


FIGURE 47. OXIDATION WEIGHT GAINS OF SILICIDE-COATED Ta-30Cb-7.5V ALLOY AT 1200 TO 2900 F DURING CYCLIC FURNACE TESTS⁽⁴⁵⁾

TABLE 37. CYCLIC OXIDATION LIVES OF STRAIGHT SILICIDE-COATED
Ta-30Cb-7.5V ALLOY SPECIMENS IN FURNACE OXIDATION
TESTS^{(45)(a)}

Exposure Temperature, F	Oxidation Lives of Individual Specimens, hours		Room-Temperature Bend Properties of Substrate After Exposure
	Undefected	Defected ^(b)	
1200	>100, >100, >100	--	OT
1500	>100, >100, >100	--	OT
1800	>100, >100	<1, <1	OT ^(c)
2000	25-50, 50-75, 50-75	--	Embrittled
2200	>100, >100, >100	--	OT
2500	>24, >24, >24	--	OT
2700	2, 10, 12	<1, <1	--
2900	6, >17, >17	--	OT

(a) Specimens cycled to room temperature after 1, 25, 50, 75, and 100 hours at temperatures up to 2200 F; after 1, 3, 7, 11, 15, 19, 20, 22, and 24 hours at 2500 F; at 1-hour intervals at 2700 and 2900 F.

(b) 0.020-inch-diameter hole drilled through coating on one side of the sample.

(c) Defected specimens were embrittled.

TABLE 38. RESULTS OF CYCLIC OXYACETYLENE TORCH
OXIDATION TESTS OF SILICIDE COATING
ON Ta-30Cb-7.5V^{(a)(45)}

Test Temperature ^(b) , F	Number of 1/2-Hour Cycles	Observation
3000	2	Failed at 3180 F
3000	4	Failed by cratering
2700	>10	Did not fail
2500	>10	Did not fail
1800	>10	Did not fail

(a) Samples were 0.040 by 0.5 by 2-inch flat sheet. Torch flame was positioned normal to the sheet.

(b) Uncorrected, optically determined.

TABLE 39. TENSILE PROPERTIES OF SILICIDE-COATED Ta-30Cb-7.5V ALLOY 40 MILS THICK⁽⁴⁵⁾

Specimen Geometry	Condition ^(a)	Test Temp, F	0.2% Offset Yield Strength, ksi ^(b)	Ultimate Tensile Strength, ksi ^(b)	Elongation in 1 Inch, per cent
Unnotched	Uncoated	RT	92.0	106.0	>20
Unnotched	Uncoated; 16 hours at 2200 F in vacuum (simulated coating treatment)	RT	83.6	100.3	26
Unnotched	Coated	RT	85.7	105.4	13
Unnotched	Coated and exposed 1 hour at 2700 F in air	RT	85.4	102.4	20
Unnotched	Coated and strained 1.5% in 1/4 hour at 2200 F in air	RT	87.6	104.6	27
Notched ^(c)	Uncoated; 16 hours at 2200 F in vacuum (simulated coating treatment)	RT	--	105.1	3-4
Notched ^(c)	Coated	RT	--	107.0	3-4
Notched ^(c)	Coated and exposed 1 hour at 2700 F in air	RT	--	102.6	3-4
Unnotched	Uncoated	2200	30.5	36.5	85
Unnotched	Uncoated; 16 hours at 2200 F in vacuum	2200	38.3	39.6	56
Unnotched	Coated ^(d)	2200	47.6	50.3	38

(a) All specimens recrystallized by annealing 1 hour at 2200 F in vacuum prior to the treatments listed.

(b) Strengths based on area of substrate core only; data were corrected for substrate consumed during coating formation.

(c) Center-hole notch with a calculated stress-concentration factor of 2.3.

(d) Single specimen, all other values are averages of two specimens.

TABLE 40. OXIDATION RESISTANCE OF R-506 COATING ON TANTALUM ALLOYS IN STATIC AIR^(a) (17, 47)

Substrate	Oxidation Temperature, F	Time to Coating Failure, hr
Ta-30Cb-7.5V	2800	1
Ditto	2800	5
"	2800	3
Ta-10W	2800	>8
Ta	2600	30
Ta-30Cb-7.5V	1800	213
Ta-10W	1800	221
Ta-30Cb-7.5V	1100	221
Ta-10W	1100	24

(a) Coatings were 1, 2 to 3 mils thick.

COATINGS FOR TUNGSTEN

Thompson Ramo Wooldridge and General Telephone & Electronics are conducting the only Government-sponsored research programs on oxidation-resistant coatings for tungsten. These programs have established that the maximum protective temperature for silicide coatings is 3600 F; thus, higher temperature coatings will be required to fully realize tungsten's capabilities. Considerable effort has been expended to protect tungsten from oxidation at temperatures up to 5000 F with thick metal-reinforced layers, but this lies outside the scope of this report.

(Si-W) and Ti-Zr-(Si-W) Silicide Coatings⁽²⁾

Thompson Ramo Wooldridge is developing two silicide coatings for tungsten which are applied by vacuum pack cementation, as described below.

(Si-W) Coating

4 hours at 2000 F in pack consisting of 1 liter of silicon sponge, 10 grams tungsten powder, and 20 grams NaF.

Ti-Zr-(Si-W) Coating

(Cycle 1) Titanium deposited in 10 hours at 2000 F in pack containing titanium sponge and NaF.

(Cycle 2) Zirconium similarly deposited at 2000 F.

(Cycle 3) Same as the (Si-W) coating process described above.

The Ti-Zr coating layer is about 1 mil thick, and after siliconizing the coatings range in thickness from 3 to 5 mils. The coatings frequently receive an oxide conversion treatment in water-saturated hydrogen (72 F) for 2.5 hours at 2200 F to form a thin surface oxide, in which case the coating designations become (Si-W)-O or Ti-Zr-(Si-W)-O.

The coating procedure for the Ti-Zr-(Si-W) coating has not been optimized yet. The principal problem has been formation of an undersirable "crust layer" on the coating surface during the (Si-W) coating cycle which causes accelerated oxidation failure. The simple (Si-W) coating is relatively easy to apply, and conditions for applying it have been standardized.

The oxidation resistance of the two coatings in cyclic furnace tests is summarized in Table 41. Both systems exhibit accelerated coating oxidation at 1600 and 1800 F, forming a nonprotective, powdery, porous oxide. The oxidation mode appears to be similar to that described by Pranatis et al. (6) as occurring with straight WSi_2 coatings on tungsten at comparable temperatures. The popular term for this phenomenon is pest. Vitreous oxide forms at temperatures greater than 2500 F, and substantial protection is provided by the coatings at temperatures from 2500 to 3600 F. The coatings are not protective at 3650 F. Substrate delaminations are a common cause of premature coating failures at all temperatures. Chemical reaction with ceramic supports sometimes causes premature failures at temperatures above 3000 F. Generally, both coatings exhibit similar capabilities for oxidation protection.

TABLE 41. OXIDATION PERFORMANCE OF TRW SILICIDE COATINGS ON 60-MIL TUNGSTEN SHEET IN CYCLIC FURNACE TESTS^(a) (2)

Test Temperature, F	Coating	Time to Coating Failure, hr
1600	Si-W	1 hr max
	Ti-Zr-(Si-W)-O	3 hr max
1800	Si-W	10 - 50
	Ti-Zr-(Si-W)-O	1.5 - 25
2500	Si-W	30 - 50
	Ti-Zr-(Si-W)-O	3 - 40
3000	(Si-W)-O	10 - 47
	Ti-Zr-(Si-W)-O	20 - 72
3300	(Si-W)-O	8
3300	Ti-Zr-(Si-W)-O	4 - 25
3450	(Si-W)-O	1 - 8
	Ti-Zr-(Si-W)-O	1 - 17
3500	(Si-W)-O	3 - 7.5
	Ti-Zr-(Si-W)-O	2 - 5
3600	(Si-W)-O	1 hr max
	Ti-Zr-(Si-W)-O	1.5 hr max
3650	(Si-W)-O	A few minutes
	Ti-Zr-(Si-W)-O	A few minutes

(a) Oxidation tests were conducted in still air. Specimens generally cycled to room temperature once every 3 hours at and below 2500 F, and once each hour above 2500 F.

The performance of the coatings in thermal-shock and hot-gas-erosion tests is described in Table 42. Again the coatings appear to behave similarly.

Tensile properties of uncoated, coated, and coated-and-oxidized tungsten sheet specimens are presented in Figure 48. Uncoated material was tested in both wrought and recrystallized conditions. The thermal treatment associated with applying the Ti-Zr-(Si-W)-O coating recrystallized the substrate (except for a thin surface layer), but the (Si-W) coating treatment (no preoxidation treatment) did not result in recrystallization. In general, the yield and tensile strength values obtained reflected the residual cold work in the substrate; in general the coatings appeared to have only minor effects, except perhaps at room temperature where low fracture strengths suggest extreme embrittlement effects. Ductility was essentially nil at room temperature for uncoated and coated specimens, but it was about 10 per cent at 1000 F and it increased further at temperatures above 2000 F.

In conclusion, the tests conducted to date have not indicated which of the two coating systems is better.

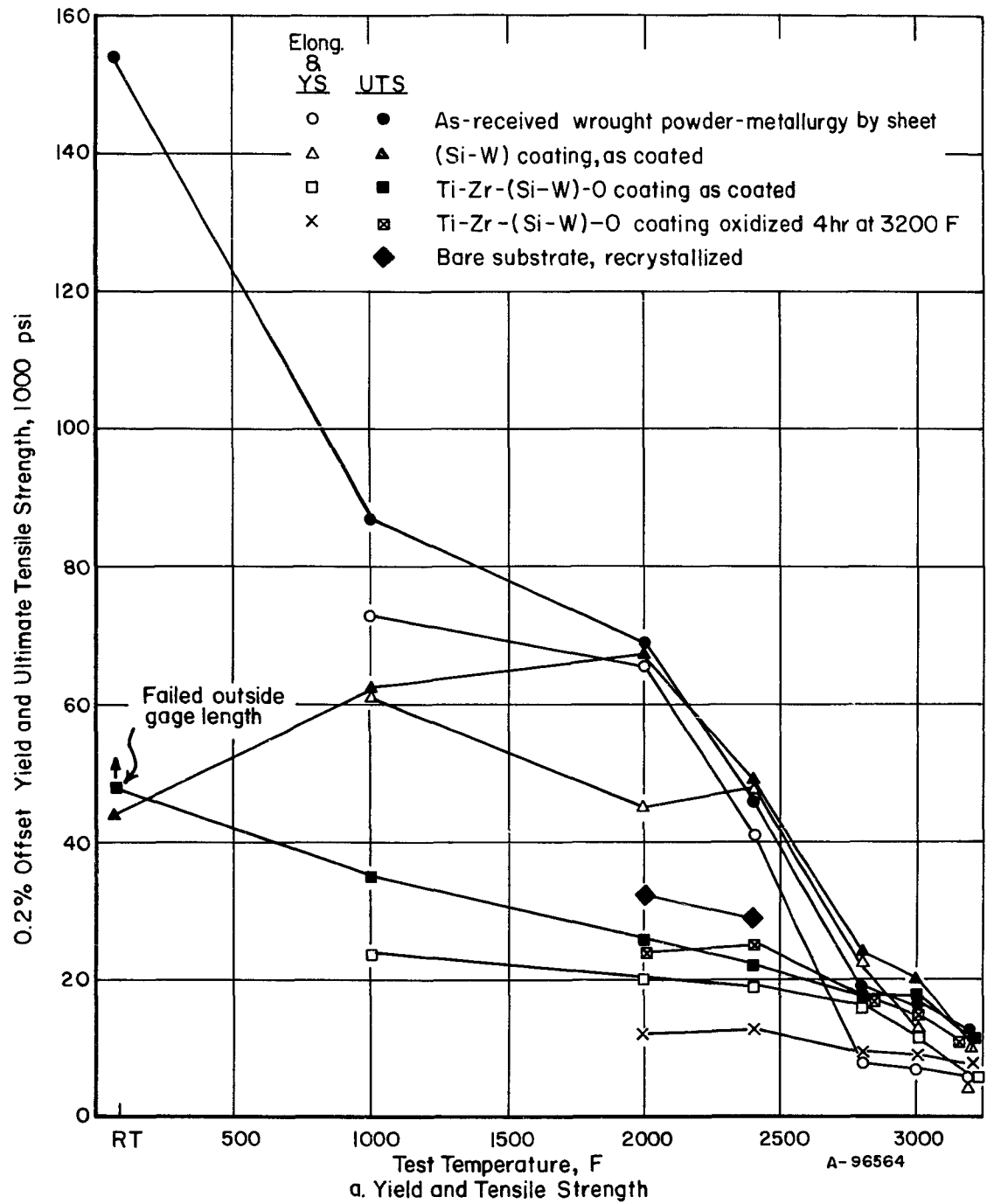


FIGURE 48. TENSILE PROPERTIES OF UNCOATED AND COATED 60-MIL TUNGSTEN SHEET TESTED IN INERT ATMOSPHERE⁽²⁾

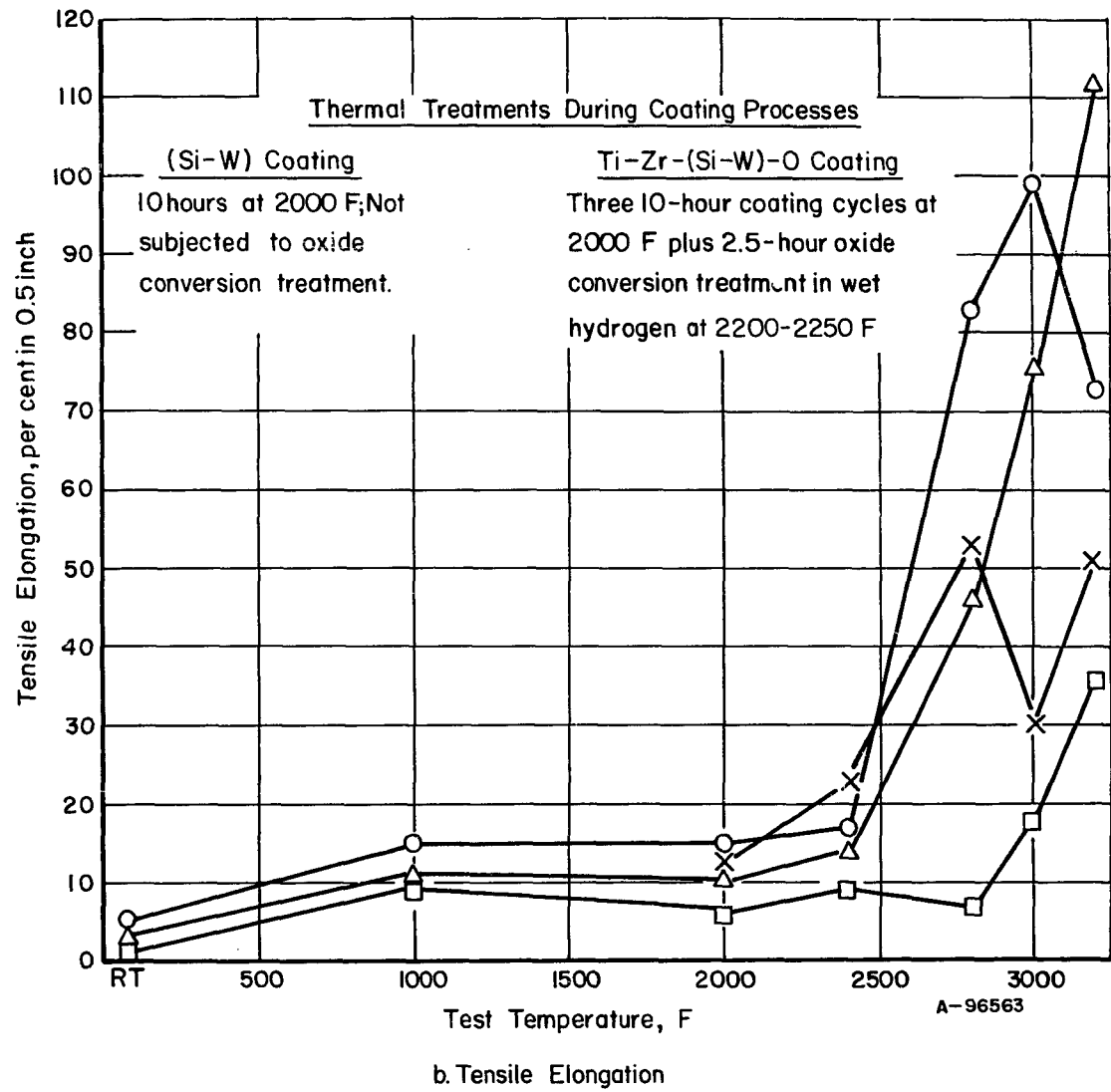


FIGURE 48. (CONTINUED)

TABLE 42. PERFORMANCE OF (Si-W)-O AND Ti-Zr-(Si-W)-O COATINGS^(a) ON 60-MIL TUNGSTEN SHEET IN THERMAL-SHOCK AND HOT-GAS-EROSION TESTS⁽²⁾

Thermal-Shock Tests ^(b)			
Test Temperature, F	Prior Oxidation Exposure	Coating	Number of Cycles to Coating Failure
2000	--	(Si-W)-O	1000
2000	--	Ti-Zr-(Si-W)-O	1000
2500	--	(Si-W)-O	372
2500	--	Ti-Zr-(Si-W)-O	465
2800	--	(Si-W)-O	250
2800	--	Ti-Zr-(Si-W)-O	310
3000	--	(Si-W)-O	365
3000	--	Ti-Zr-(Si-W)-O	241
3000	0.5 hr at 3000 F	(Si-W)-O	>100
3000	0.5 hr at 3300 F	(Si-W)-O	>100
3000	1 hr at 3000 F	Ti-Zr-(Si-W)-O	>50
3200	--	(Si-W)-O	200
3200	--	Ti-Zr-(Si-W)-O	211
Hot-Gas Erosion Tests ^(c)			
Test Temperature, F	Coating	Time to Failure, hr	
3200	(Si-W)-O	2	
3200	Ti-Zr-(Si-W)-O	2	
3400	(Si-W)-O	1.7	
3400	Ti-Zr-(Si-W)-O	2	

(a) Test specimens were 1-inch-wide by 2-inch-long pieces of 60-mil tungsten sheet, curved to a 3/16-inch radius.

(b) Thermal-shock test procedure: Specimens heated on the front side to the test temperature with an oxyacetylene torch in 20 seconds and then cooled to 250 F with an air blast in 10 seconds.

(c) Procedure for hot-gas erosion test: Specimens exposed to effluent of a plasma-arc torch having an exit-gas velocity of 2000 ft/sec and a composition of 20 per cent oxygen and 80 per cent nitrogen.

R-507A Coating⁽⁴⁸⁾

General Telephone & Electronics has a coating for tungsten, designated R-507A, which is applied by pack-cementation siliconizing followed by a proprietary coating process. The coating subsequently is heated in air at an elevated temperature to serve as a combined diffusion and preoxidation treatment. Coating lives of 18 to 40 hours have been obtained when the maximum temperature of resistance-heated rod specimens was 3450 F. Failures occurred by pest, however, in the zone that was between 2200 and 2500 F. The coating was protective for 4 to 8 hours at 3450 F in an oxyacetylene-torch test.

DISCUSSION

Evaluation of the performance data that are available for coating systems to define the relative merits of various coatings still is quite difficult, although the situation has improved within the past 2 or 3 years. Several problems complicate proper interpretation of the available data. Test procedures used by various investigators frequently are different; the appropriate direction should be toward standardized tests. To this end, the Materials Advisory Board has published a report describing standard tests that it advocates⁽⁴⁹⁾. Most technologists want to be able to compare the mechanical properties of coated substrate with those of uncoated substrate. Ideally the bare substrate should be exposed to the "coating thermal treatment" and then tested under the same conditions as coated specimens, so the effect of the coating can be isolated. Frequently the thermal history of the substrate prior to coating (i. e., stress-relieved wrought structure or recrystallized) or the coating thermal treatment is not given in test data. If not specified, it generally has been assumed in this report that as-received material was in the stress-relieved condition. Thermal history of test specimens is important, because coating and subsequent oxidation treatments frequently transcend the recrystallization temperature. For instance, a comparison of the tensile strength of stress-relieved bare substrate with recrystallized coated substrate would be nebulous. Frequently it is not specified how the cross-sectional area of coated specimens is obtained for calculating strength. The most common method is to use the dimensions of a sheet tensile specimen prior to coating. It has been assumed, unless specified otherwise, that this method was used for calculating the strength data in this report. Another method is to measure the residual substrate thickness metallographically and use it to calculate strength. The first method usually results in "apparent" strength values for coated substrate which are below those for uncoated substrate. The "change in strength" values calculated by the two methods diverge as sheet thickness decreases. Sheet thickness is decreased by up to 1 mil per side by diffusion formation of coatings, so the residual substrate thickness is as much as 2 mils less than the uncoated substrate. The 2-mil thickness reduction would amount to a 5 and 20 per cent reduction in cross-sectional area, respectively, for 40- and 10-mil sheet. Of course there could be some concurrent diffusion strengthening of the substrate by the coating elements.

Performance of a particular coating can be good or poor depending on test conditions, making it uncertain in some instances whether the coating is hypersensitive to test procedures or reproducibility of the coating is poor. Many coatings are standardized, but variations in thickness, intentional or unintentional, and other variables, frequently becloud analysis of data.

Occasionally some of the coatings described in this report have demonstrated different oxidation resistance on different alloys, even though the alloy base was the same (e.g., columbium-base alloys, tantalum-base alloys). The finding by Battelle that the substrate elements occur in silicide coatings on tantalum-base alloys in approximately the ratio of their occurrence in the substrate offers an explanation. Oxidation behavior is sensitive to the composition of a coating. Hence a given coating might provide different oxidation resistance on two different alloys because of the existence of the substrate alloying elements in the coating. Several examples are contained in this report that show the desirable influence of titanium in the columbium-base substrate on performance of the coating. The radically different performance of the Vought coating on D14 and FS85 columbium alloys also suggests an important effect of substrate.

Generally it is the ductility of a substrate rather than strength that is degraded most by coatings. This can be described as a manifestation of an increase in the ductile-to-brittle transition temperature by the coating and/or the coating thermal cycle. The question arises as to whether the tensile or bend test is the best method for ascertaining the ductility of coated material. In the work at Solar on testing coated foil, several coatings resulted in nil tensile ductility of the substrate but did not cause specimens to fracture in a 4T bend test (which requires a nominal outer fiber elongation of 10 per cent). Part of the difficulty with bend tests undoubtedly is in differentiating a coating crack from a substrate surface crack, the latter signaling specimen failure according to MAB test procedures established for uncoated refractory metals⁽²²⁾. In view of the apparent hypersensitivity of the tensile test for detecting substrate embrittlement by a coating, and the more quantitative nature of the test data obtained, it appears that the tensile test is superior for detecting embrittlement. In addition the yield and tensile strength data obtained conjunctively in the test are of paramount importance in any coating-evaluation program.

In conclusion, despite difficulties in the analysis of data, information generated within the past 2 years describes, to a considerable extent, the relative behavior of various coatings for columbium and molybdenum and their alloys. Some of the more recent evaluation programs have been able to utilize the growing wealth of data to minimize the selection of coating-substrate systems for more detailed evaluation. It is anticipated that current and future programs will continue to define the behavior of coated systems to further simplify the task of selecting the best coating for a given application.

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46D	Department of Defense Titanium Sheet-Rolling Program - Uniform Testing Procedure for Sheet Materials, September 12, 1958 (PB 121649 \$1.25)
46E	Department of Defense Titanium Sheet-Rolling Program - Thermal Stability of the Titanium Sheet-Rolling-Program Alloys, November 25, 1958 (PB 151061 \$1.25)
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109	Coatings for Protecting Molybdenum From Oxidation at Elevated Temperature, March 6, 1959 (PB 151064 \$1.25)
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118	Welding of High-Strength Steels for Aircraft and Missile Applications, October 12, 1959 (PB 151074 \$2.25)
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185	The Status and Properties of Titanium Alloys for Thick Plate, June 14, 1963
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192	Hot-Cold Working of Steel to Improve Strength, October 11, 1963
193	Tungsten Research and Development Review, October 23, 1963
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